Bending Gold Nanorods with Light

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Plasmonic metasurfaces: 2D arrays of metallic nanoresonators which exhibit collective and tunable resonance properties controlled by electromagnetic near-field coupling. These man-made surfaces are capable of manipulating light in unprecedented ways.

Metasurfaces are generally requires the custom arrangement of individual anisotropic light scatterers (such as optical antennas) with controlled shape and orientation.

The spacing between antennas and their dimensions are much smaller than the wavelength. As a result the metasurfaces are able to mould optical wavefronts into arbitrary shapes with subwavelength resolution to exhibit unique optical properties.

(SEM) image of a metasurface consisting of an array of V-shaped gold optical antennas fabricated on a silicon wafer.

Flat optics with designer metasurfaces
Nanfang Yu & Federico Capasso
Nature Materials 13, 139–150 (2014)
Optical printing: an alternative to lithography

- **Experimental setup**: Up-right optical microscope that combines dark-field detection in wide field and confocal sample scanning with CW lasers.
- The substrates are surface functionalized with negative charges using layer-by-layer deposition of polyelectrolytes to avoid spontaneous binding of the NPs.
- The focused laser beams generate optical forces on the NPs that push them toward the beam center and toward the substrate. Above a certain laser intensity the electrostatic repulsion from the substrate is surpassed and the NPs are printed. The printing process was computer controlled and fully automated.

Each printing event is detected as an increase in the scattered light signal on the corresponding confocal channel.

Upon detection of a printing event, the laser illumination is immediately blocked, the sample is moved to the next printing position with a piezoelectric nanopositioning stage, and the laser is unblocked until the next printing event occurs.
Plasmonic metasurfaces made of “V-shaped” gold nanoantennas display two orthogonal plasmonic resonances which are determined by the opening angle and the length of each antenna branch.

Both resonances can be excited by light with a corresponding wavelength and polarization and the combination of both modes allows to induce phase shifts between incoming and scattered light over the full range of $2\pi$.

Challenges: small size and complexity of the antenna structures demand the use of high-end nanofabrication methods. Also chemical synthesis of V-shaped particle remains a challenge.

Studies: the transition from a gold rod to a sphere starts at the interior of the rod by the creation of point and line defects, which eventually leads to the formation of planar stacking defects and twinning. This is followed by the surface diffusion of gold atoms from the tips to the center of the rod.

Here they report that combination of optical forces and plasmonic heating renders it possible to bend gold nanorods and simultaneously print them on the surface of a flat substrate.
(a) Gold nanorods are diffusing in solution (step 1). A single rod aligns horizontally as soon as it enters the laser focus (step 2). The nanoparticle is heated in the laser beam, while optical forces simultaneously push the particle toward the substrate (step 3).

(b) Bending angle of the printed particles can be controlled by the laser power density. Optically printed gold nanorods display a transition from a straight (*) to a bent (**) morphology above a laser power density of 0.45 MW/cm². The Red dotted line: the laser power density required to heat the nanorods above their melting temperature according to simulations.

(c) SEM images of gold nanorods that were printed with different bending angles.

Figure 1. Optical bending and printing of gold nanorods.
The bending phenomenon

✓ A gold nanorod aligns perpendicular to the Poynting vector when it diffuses into the laser beam. In this position, the rod is pushed in the direction of the beam propagation by the optical force. This causes hydrodynamic pressure on the rod, which is working in the opposite direction of its movement.

✓ Solving the Navier-Stokes equations regarding the distribution of the hydrodynamic pressure along the long axis of a horizontally aligned nanorod indicates: pressure is almost 30% stronger at the tips compared to the center.

✓ Assuming that the heated rods are to some degree soft and deformable, this pressure difference then leads to a symmetric deformation of the linear structure. The bending occurs primarily in the center region of the rod.

✓ Bending starts at a laser power that produces sufficient heat to melt gold.

✓ No bending was observed for rods that were attached to the substrate, potentially because no movement of the particles was involved during heating.

✓ Both, the peak positions of the absorption and scattering cross section of the bent structures are decreasing and blue-shifted for a smaller bending angle. That leads to a less efficient heating and weaker optical forces. For strong bending deformation, the particle temperature could eventually drop below the melting point, which causes the particle to freeze instantaneously.

✓ The controlled deformation might be due to the use of CW laser instead of pulsed laser.
Figure 2. Optical properties of bent gold nanorods.

(a) Polarization-dependent Rayleigh scattering spectra of a single V-shaped gold particle (104°)

Two peaks @ 700 and 1000 nm correspond to a “symmetric” (black curve) and an “antisymmetric” (blue curve) plasmon resonance with respect to the symmetry axis of the structure.

Both modes can be separately excited with polarized light.

Both plasmon resonances are visible if the particle is excited with polarized light at a 45° angle (red curve).

Background scattering: deviation from perfect V shape.

(b) Polarization dependence of both peaks.

(c) FDTD simulations of the near-field enhancement and charge distribution in a bent GNR for symmetric and antisymmetric excitation with polarized light.

(d) Simulations of the polarization dependent scattering spectra of a bent gold nanorod with 105° opening angle.

colored scale bar: enhancement factor of electromagnetic field with respect to initial incident light.
Figure 3: STEM study of crystal changes in V-shaped Nanoantennas

(a) STEM image of a straight gold nanorod. The rod is elongated parallel to the \( <100> \) direction. No defects are observed in the crystal structure. (b) STEM image of a bent gold nanorod. The branches of the nanorod still display the crystallographic orientation of a straight rod. (c) Colored STEM image of twin domains (twin planes indicated in white) in the bent area with corresponding (color code) FFT. The green and cyan areas have equivalent crystal orientation. (d) High resolution HAADF-STEM image of the twin structure (marked by the tilted \( \{111\} \) planes). After printing, the bent nanorods remain crystalline.

This observation is in good agreement with the findings of previous studies and with molecular dynamic simulations of FCC nanowires, reporting that the deformation in a single FCC crystal is possible due to twin formation along the \( \{111\} \) crystal planes.
(a) Simulation of the hydrodynamic pressure along a gold nanorod that is moving in water at a speed of 0.02 m/s. The line of black arrows highlights the relative intensities of the pressure at different positions along the rod. A higher hydrodynamic pressure is observed at the tips compared to the middle part. (b) FDTD simulations of the absorption cross sections of gold nanorods with different bending angles. A smaller bending angle leads to a decrease of the absorption cross section and a blue shift of the absorbance maximum, which results in less efficient heating at $\lambda = 1064$ nm.

Blue shift of the ASPR peak compared to the calculated value from FDTD:
The bent rod was still heated by the laser after it was already printed to the glass substrate. Therefore, the rods start to melt at the tips, reducing the effective length of plasmon propagation while there is no further change of the bending angle.
Simulations of the scattering force for different laser power densities. The red dashed lines in all three plots represent the position where the calculated particle temperature is the melting temperature of gold. The corresponding scattering force at this position is shown for each plot. An example for the temperature of a straight gold nanorod at different positions along the laser beam is shown in the left panel. Absorption cross sections of $3.88 \times 10^{-14}$, $3.79 \times 10^{-14}$, and $3.47 \times 10^{-14}$ m$^2$ were used to calculate the temperature for rods with a bending angle of 180°, 150°, and 120°, respectively.

With higher laser powers, both the particle temperature and optical forces are increasing. The nanorods thus remain deformable over a distance of several micrometers away from the laser focus and are, at the same time, subject to a stronger hydrodynamic pressure. Both factors therefore result in a stronger bending deformation.
Figure 5. Orientation control by optical printing with linear polarized light: A statistical analysis of the orientation of the printed straight and bent nanorods.

(a) SEM image of a line of five optically printed, V-shaped nanorods. (b-d) Histogram analysis of the nanorod orientation of the printed nanorods with respect to the laser polarization. The (0,0) direction depicts the orientation of the polarized laser beam; 50 nanoparticles were measured for each histogram. (b) Angular deviation of straight nanorods printed with polarized light. (c) Angular deviation of bent nanorods with opening angle of 136°, and (d) with an opening angle of 118°. Sigma = oriental precision.

✓ A preferential alignment of the particles is feasible, although the precision appears to become slightly more inaccurate with the high bending deformation.
✓ Modifying the shape of the laser beam or tilting the substrate on one side are possible strategies that will likely allow to have a better control over the angle orientation.
Gold nanorods can be bent in a controlled way by means of light.

The combination of optical forces and plasmonic heating renders it possible to adjust the bending angle of single gold nanorods by changing the laser power.

Nanorod bending along with hydrodynamic pressure determines the degree of deformation and it has immediate consequences on the plasmonic properties of the particles.

Bending was only observed for particles that were freely diffusing in solution. This illustrates that a combination of particle movement and melting transformation is required to control the overall process.

Straight as well as bent particles can be printed optically onto a glass substrate. Using polarized laser light allows controlling the alignment of the nanorods on the surface.

This new approach renders it possible to generate arrays of bent or “V-shaped” nanoantennas and to assemble them in a controlled orientation on top of a solid support, which holds great potential for the fabrication of flat optics and metasurfaces in the future.
• The diameter of the laser beam was measured to be 651 nm at FWHM.
• Each laser power was measured with a powermeter directly after the water-immersion objective.
• Rayleigh scattering spectra of bent nanorod particles were collected with a spectrograph.
• The bent gold rods were represented as two cylinders connected by a sphere and two spheres at the end.
• **Poynting vector** represents the directional energy flux density (the rate of energy transfer per unit area) of an electromagnetic field. The SI unit of the **Poynting vector** is the watt per square metre (W/m²).
• M.P of gold = 1064 C.
• FDTD = finite difference time domain