Chiral comma-shaped gold nanoparticles: fabrication and refractive index sensitivity

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Abstract. Chiral gold nanoparticles with asymmetric crescent shape have been fabricated using the In-situ resist colloidal lithography approach. Optical properties of these plasmonic particles have been studied experimentally and using the finite-difference time-domain simulations. Nanocommas exhibit a considerable circular dichroism with high anisotropic g-factor of about 0.2. Numerically studied refractive index sensitivity of the material has been demonstrated.

1. Introduction
Chiral metamaterials have been attracting a lot of attention in the past decade, due to the interesting and promising optical properties, such as the extraordinary high or broadband optical activity, and switchable circular dichroism [1]. A large number of materials with different 2D and 3D particles have been studied so far, indicating the importance of using the accurate fabrication methods to exploit the tunability of their optical properties. Besides, practical application of chiral metamaterials relies upon robustness and cost-efficiency of the fabrication process. In this work we demonstrate the fabrication of comma-shaped 2D chiral gold nanoparticles using the self-assembly based colloidal lithography approach, followed by the results of experimental and numerical investigation of their optical properties.

2. Fabrication
Chiral plasmonic crescent nanostructures have been fabricated using the in-situ resist colloidal lithography (IRCL) approach [2]. In this method, sulfate latex microspheres are electrostatically adsorbed onto a substrate covered by triple polyelectrolyte layer; then a series of glancing-angle deposition (GLAD) steps is needed to produce nanostructures with desired shape. Each microsphere serves as a lithographic mask in further vacuum deposition process. A distinctive feature of IRCL is the deposition of a dielectric resist layer, which patterns the substrate’s surface prior to the metal deposition. Particularly, silica has been successfully used as a such resist to define the areas for further deposition of gold.

For the fabrication of comma-shaped particles, 300 nm latex sulfate particles have been used. Then, after 5 min UV/ozone oxidation, 25 nm of silica resist layer has been deposited at a glancing angle of 40°. After that, the substrate has been turned by 90° around the normal axis and 20 nm of gold has been deposited at 35°.

Latex microspheres and the top layer of gold have been removed after taking samples to air by multiple tape-stripping. The remaining gold nanoparticles were located inside the holes in silica film.
3. Optical properties
Optical properties of comma-shaped nanoparticles have been studied using the UV-vis-NIR spectroscopy, circular dichroism spectroscopy and finite-difference time-domain (FDTD) simulations. A considerable circular dichroism has been detected in experiment and simulations at the wavelength of the low-energy resonance mode. The CD spectrum is presented in figure 1. The corresponding value of anisotropic g-factor was about 0.2.

![Figure 1](image)

**Figure 1.** SEM image of comma-shaped gold nanoparticles (left) and their circular dichroism spectra (right) upon illumination from the top (red) and the bottom (black).

Since the calculated local electric field enhancement reaches two orders of magnitude near the sharp tip, these structures can be used for refractive index sensing. Extinction spectra of comma nanoparticle have been calculated at different refractive index of the media (see figure 2). The largest values of the peak shift have been observed for the low-energy mode peak near 1800 nm. The calculated refractive index sensitivity of this peak was about 600 nm/RIU.

![Figure 2](image)

**Figure 2.** Calculated extinction spectra of gold comma-shaped particle at different refractive index of the media

To prove the capability of such structures to detect small concentrations of biomolecules, the peak shifts induced by the presence of a small 5 nm sphere with refractive index \( n=1.5 \) near the comma surface, has been studied. The observed peak shift was 5 nm compared to the peak position without the sphere.
4. Conclusion.

Arrays of comma-shaped chiral nanoparticles have been fabricated using the IRCL technique. The structures exhibit circular dichroism and possess high anisotropy factor $g=0.2$. The particles are evenly distributed on the surface with short-range order, resembling an amorphous metasurface. Besides, these plasmonic nanostructures can be used for refractive index sensing, exhibiting sensitivity of 600 nm/RIU at ~1800 nm. The capability to detect biomolecules has been demonstrated.

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References
[1] Valev V K, Baumberg J J, Sibilia C and Verbiest T 2013 Adv Mater 25 18 2517
[2] Bochenkov V E 2017 AIP Conf Proc 1874 030004