Three-Dimensional Bichiral Plasmonic Crystals Fabricated by Direct Laser Writing and Electroless Silver Plating

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Negative refraction is a striking optical phenomenon with several promising applications, including a “superlens” with sub-wavelength resolution that, in principle, is only limited by fabrication imperfections.[1] Although negative refraction does not occur naturally, it can be attained in artificially engineered optical media, so-called metamaterials. In the original description, negative refraction was predicted for simultaneous negative values of the electric permittivity and the magnetic permeability.[2] Recently, J. B. Pendry pointed out an alternative route to negative refraction by exploiting chirality in combination with a resonant system with a photonic band gap.[3] The fundamental viability of this approach has already been demonstrated experimentally at GHz and low THz frequencies.[4,5] Since chirality is inherently a three-dimensional (3D) phenomenon, realization of this approach at optical frequencies requires a technique for fabricating sufficiently small 3D chiral structures consisting of the appropriate materials.[6] Here, we report on the fabrication and optical properties of 3D bichiral plasmonic crystals which were fabricated by 3D direct laser writing and subsequent electroless silver plating.

M. Thiel et al. fabricated chiral photonic crystals consisting of 3D dielectric (photoresist) helices arranged vertically on a two-dimensional (2D) square lattice.[7] Transmittance measurements for circularly polarized light propagating along the helix axis found stop bands when the pitch of the dielectric helices matched the wavelength of light in the dielectric. Since this structure was uniaxial, its optical properties depended strongly on the angle of incidence. In a subsequent publication, Thiel et al. presented bichiral dielectric photonic crystals with a 3D simple cubic lattice.[8] The chosen architecture was inspired by blue-phase cholesteric liquid crystals.[9-11] The photonic crystal consisted of three sets of 3D dielectric helices, one set oriented along each of the three orthogonal axes of the simple cubic lattice. To obtain mechanically stable structures, the helix axes were shifted by one helix radius so that all three helices intersected at the center of the simple cubic unit cell (see Figure 1 in Thiel et al.[8]). Since there exist two such mirror-symmetric arrangements of the helix axes, so-called left-handed and right-handed corners, as well as two choices for the handedness of the helices themselves, the crystals feature two types of chirality and are therefore called bichiral. By construction, these crystals are not uniaxial and their optical properties should be identical for light propagating along any of the three crystal axes. Stronger chiral effects over a larger frequency range are usually expected when switching from dielectric to metallic structures. In this vein, J. Gansel et al. investigated the metallic counterpart of the uniaxial photonic crystal discussed above, i.e., an arrangement of 3D gold helices on a 2D square lattice.[12,13] For light propagating along the helix axis, this structure blocks the circular polarization with the same handedness as the helices over a frequency range of over one octave, indeed a much wider range than for the dielectric original.

In this Communication, we aim to fabricate and characterize a metallic counterpart of the 3D bichiral dielectric crystals starting from the same point as Thiel et al., that is structures fabricated by direct laser writing (DLW) in a negative-tone photoresist.[8] Gansel et al. modified this approach to obtain gold helices by exposing helical cavities into a positive-tone photoresist via DLW on a conducting substrate, subsequently filling these cavities with gold by electroplating with an external current source, and finally removing the photoresist mold by plasma etching.[12] However, the latter approach turned out to be impractical for the 3D bichiral structures. During the electroplating, certain parts of the horizontally aligned helical cavities would be cut off from the electrolyte before they have been filled in completely, leaving behind gaps in the final structure.

Figure 1 illustrates our fabrication scheme. We first fabricated a 3D bichiral crystal by two-photon femtosecond DLW in a negative-tone photoresist.[14,15] Next, this dielectric template was coated with a conformal metal film via electroless silver plating. Electroless plating is a wet-chemical metallization technique based on an autocatalytic redox reaction that does not require an external current source, and thus coated all exposed surfaces. Finally, since electroless plating also coated the substrate with silver, the silvered crystal was detached with a glass capillary and transferred to a clean substrate in order to facilitate transmission spectroscopy. We note that standard deposition methods such as sputter coating or vacuum evaporation were unsuitable for metal coating due to self-shadowing of the complex 3D geometry.

When the crystal rested directly on the substrate surface during electroless plating, detaching the bottom of the crystal from the substrate afterwards created holes in the silver film at the contact points and thus artifacts in the optical spectra.
At perpendicular incidence, the crystal with left-handed corners and left-handed helices features an RCP transmittance maximum of 0.33 at a wavelength of 3.9 μm. Overall, RCP transmittance rises significantly above LCP transmittance in the wavelength range from 3.5 to 4.7 μm. Throughout this range, LCP transmittance remains below 0.15 and the maximum difference in transmittance is 0.26. As expected from symmetry, the crystal with right-handed corners and right-handed helices shows largely similar transmittance spectra, except that the spectra for LCP and RCP are exchanged. In contrast to these two crystals with pure chirality, the crystal with left-handed corners and right-handed helices demonstrates a significant enhancement in RCP transmittance over LCP transmittance in the specified wavelength range.

Therefore, the photonic crystal was stood off of the substrate with vertical posts which served as spacers between the crystal and the substrate, one at each crystal corner. During electroless plating, the posts prevented direct contact between crystal and substrate. As a further benefit, the posts served to simplify detaching the crystal from the substrate by functioning as predetermined breaking points.

Figure 2 displays a selection of scanning electron microscopy (SEM) images and optical micrographs of our bichiral crystals taken after electroless silver plating. The oblique and top views demonstrate excellent structural fidelity (Figure 2a,c). The cross section obtained via focused ion beam milling proves that the conformal silver film also extends to the inside of the crystal (Figure 2b). The silver film is slightly granular but contiguous and contains few holes. The absence of large silver nodules is compatible with the observation that our silvering solution remained clear and colorless during electroless plating, indicating that the formation of free-floating silver clusters was sufficiently suppressed. No charging effects were observed while taking the scanning electron micrographs. The optical micrograph was taken after transferring the crystal to a new substrate and confirms the absence of any large scale damage due to handling (Figure 2d). In addition, we remark that silver films deposited on a planar substrate showed a high reflectivity and a specific conductivity of approximately 25% of the literature value for bulk silver.[16] VIS-NIR ellipsometry indicated a Drude-like dielectric function and no sign of particle plasmons due to granularity (not shown).

Panel (a) of Figure 3 shows detailed SEM images of silvered bichiral crystals with all four combinations of left-/right-handed corners and left-/right-handed helices. In panel (b) we present the corresponding transmittance spectra for left-handed circularly polarized light (LCP) and right-handed circularly polarized light (RCP) and for angles of incidence from 0° to 15°, increasing from top to bottom. In panel (c) we plot the corresponding difference of the respective angle-dependent RCP and LCP transmittance spectra.

At perpendicular incidence, the crystal with left-handed corners and left-handed helices features an RCP transmittance maximum of 0.33 at a wavelength of 3.9 μm. Overall, RCP transmittance rises significantly above LCP transmittance in the wavelength range from 3.5 to 4.7 μm. Throughout this range, LCP transmittance remains below 0.15 and the maximum difference in transmittance is 0.26. As expected from symmetry, the crystal with right-handed corners and right-handed helices shows largely similar transmittance spectra, except that the spectra for LCP and RCP are exchanged. In contrast to these two crystals with pure chirality, the crystal with left-handed corners and right-handed helices
and left-handed helices mirrors this behavior with LCP and RCP exchanged. For increasing angles of incidence, the general shape of the transmittance spectra of all four crystals remains broadly similar to those for perpendicular incidence, with the most noticeable changes in the spectra for the purely right-handed crystal.

In conclusion, 3D metallic bichiral crystals were successfully fabricated via direct laser writing and electroless silver plating helices features a lower RCP transmittance maximum of 0.22 at a wavelength of 3.3 μm. RCP transmittance rises above LCP transmittance in the smaller wavelength range from 3.0 to 3.6 μm wherein LCP transmittance remains below 0.13 and the maximum difference in transmittance is 0.09. Outside of this range, LCP and RCP transmittance do not differ significantly. Again as expected from symmetry, the crystal with right-handed corners and left-handed helices mirrors this behavior with LCP and RCP exchanged. For increasing angles of incidence, the general shape of the transmittance spectra of all four crystals remains broadly similar to those for perpendicular incidence, with the most noticeable changes in the spectra for the purely right-handed crystal.

In conclusion, 3D metallic bichiral crystals were successfully fabricated via direct laser writing and electroless silver plating.
for the first time. Measurements on crystals with purely left-handed or purely right-handed corners and helices showed large difference in transmittance between LCP and RCP with preferential transmission of circularly polarized light of the opposite handedness in the wavelength range of 3 to 5 μm. The difference in transmittance is smaller and limited to a narrower wavelength range in crystals with disparate handedness of corners and helices. These results agree qualitatively with previously published results for dielectric bichiral crystals and uniaxial gold helix arrays.\[^{[8,12]}\] Furthermore, our metallic bichiral crystals with purely left-handed or purely right-handed chirality feature a spectral region of significant difference in LCP/RCP transmittance with a relative bandwidth \(\Delta \lambda / \lambda = 29\%\) compared to \(\Delta \lambda / \lambda = 14\%\) in the dielectric case investigated by Thiel et al., even though we used only two rather than seven unit cells in the vertical direction.\[^{[9]}\] We also confirmed experimentally that transmittance depends only weakly on the angle of incidence. Electromagnetic simulations would be helpful for a deeper understanding of the optical properties of our bichiral plasmonic crystals but are beyond the capabilities of current simulation tools. A coupled oscillator model\[^{[17,18]}\] which also takes spatial dispersion into account could also allow new insights into the design and optical properties of chiral metamaterials. Our fabrication method opens a route towards very complex 3D plasmonic structures in the optical range, for example toroidal structures\[^{[19,20]}\] with completely uncommon and novel types of optical resonances.

**Experimental Section**

**Direct Laser Writing:** Detailed descriptions of direct laser writing (DLW) via two-photon absorption in general as well as the DLW setup and fabrication process with the commercially available negative-tone photore sist SU-8 used here have been published previously.\[^{[14,15,21]}\] Typical writing times were 25 minutes for a single bichiral crystal. **Electroless Silver Plating:** Immediately after development (i.e., without drying), the substrate was dipped into a tin(tetrachloride solution (0.1 M SnCl₂ and 0.1 M HCl in ultrapure water) for two minutes and thoroughly rinsed in deionized water. The adsorbed tin ions served as seeds for the subsequent autocatalytic deposition of silver by immersion in the plating solution for 30 minutes.\[^{[22]}\] Finally, the sample was rinsed in deionized water again and left to dry in a laminar air flow. **Sample transfer:** The substrate was mounted on a microscope scanning stage. A glass fiber (diameter 125 μm) or thin glass capillary (diameter 10 μm) was mounted on an adjacent manual 3D micro translation stage. The silvered crystal was detached by moving the end of the glass fiber or the side of the glass capillary in parallel to the substrate surface, thereby breaking the vertical spacer posts. The crystal usually stuck to either tool until it was deposited on a clean glass cover slip by tapping the tool very carefully.

**Measurements:** Scanning electron micrographs were taken with a LEO 1550 VP FE-SEM (Carl Zeiss SMT). Focused ion beam sections were created and imaged with a CrossBeam 1540 EsB SEM/FIB (Carl Zeiss SMT). Fourier-transform IR transmittance spectra were measured with a Vertex 80 spectrometer coupled to a Hyperion 2000 IR microscope (Bruker Optics) which was equipped with Cassegrain objectives (15x/0.4) and a liquid nitrogen cooled HgCdTe detector. The IR microscope was extended with circular polarization optics in transmission, including a custom-ordered waveplate with a retardation of \(\lambda / 4 \pm 14\%\) at wavelengths from 2.5 to 7.0 μm (B. Halle Nachfl.). The illuminating light cone was reduced to a full opening angle of 10° by introducing a circular aperture into the beam path. Adjustable knife-edge apertures in an intermediate image plane limited the measurement region to the crystal itself. The sample was mounted on a goniometer stage for angle-dependent measurements. All transmittance spectra were normalized with respect to the bare glass substrate which becomes opaque at wavelengths above 5.5 μm.

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