In the past ten years, advances in (planar) nanofabrication schemes have opened up the path for photonic nanostructures that offer unique light-manipulation functionalities. On one hand, the opportunity of using metamaterials to realize novel effects like a magnetic response at optical frequencies, a negative refractive index, and sub-wavelength imaging have led to the development of novel nanostructures, paving a way towards metamaterial circuitry and metadevices.[3] On the other hand, the ability of plasmonic nanoantennas to strongly enhance the interaction of light with nanoscale matter has stimulated tremendous progress regarding their use for efficient quantum-light sources, light harvesting, and single-molecule detection.[2] However, being restricted to mainly two-dimensional designs in the near-infrared (NIR) and visible spectral region, a broad range of effects and functionalities based on three-dimensional designs have so far been inaccessible for functional devices in the NIR. Hence, huge advances can be expected from nanoscale plasmonic metamaterials and optical nanoantennas entering the third dimension: For example, 3D metamaterials can be engineered to provide an isotropic, or tailored anisotropic, magnetic response,[3,4], while 3D nanoantennas will allow transferring some of the most efficient and successful 3D RF antenna geometries like helical and dish antennas to the nanoscale. Furthermore, 3D nanoscale plasmonic structures can be used to exploit magnetic coupling effects and, in particular, 3D chiral structures allow for efficiently manipulating the complex polarization state of light.[5–7] In addition, 3D plasmonic geometries offer the possibility to exploit several other dimensionality effects like nanofocusing by 3D plasmonic tapers[8] or fundamental dimensionality effects in fractal antenna structures.[9]

Inspired by these intriguing effects and applications, different approaches for 3D metal submicron- and nanostructure fabrication have been presented in the literature, including direct laser writing (DLW) in combination with a subsequent metalization procedure,[6,10–12] membrane projection lithography (MPL),[4] multistep electron-beam lithography (EBL),[5,7,13–15] and electron-beam deposition (EBD).[16] However, despite recent progress, the fabrication of designed high-quality 3D metal nanostructures for near-infrared frequencies still poses a major challenge due to the required sub-100 nm feature sizes: While DLW allows for the creation of almost arbitrary complex 3D structures,[4,5] the feature sizes obtained via DLW and metallization are still too large for applications in the visible or near-infrared spectral range. Although STED[19,20] and SPIN[21,22] techniques might be able to overcome this issue in the future, most DLW based approaches furthermore suffer from difficulties to metallize only the DLW template while keeping the substrate uncovered by metal,[11,23] not to mention that a controlled selective metalization of only desired parts of the DLW photoresist template has not been demonstrated so far. MPL has similar limitations in the achievable feature sizes, and is technologically extremely demanding with 12 individual fabrication steps to be performed.[4] Multistep EBL approaches, on the other hand, are limited to stacked geometries and in the number of layers achievable. Finally, methods based on EBD are affected by problems regarding the purity, and hence the optical quality of the deposited metal.

As a result, the vast majority of metamaterial and nanoantenna studies up to date have been limited to planar geometries, which are readily accessible by electron-beam lithography (EBL) in combination with metal evaporation and a lift-off procedure.[24] In this work, we suggest and demonstrate a new hybrid fabrication approach combining DLW with EBL metal nanostructure fabrication. Combining these two commercially available techniques, which can be considered the standard techniques for 3D submicron and 2D-nano rapid prototyping, respectively, we can make use of the 3D writing capability of DLW, while preserving the sub-100 nm feature sizes, the capability of selective metallization, and the excellent metal (e.g., gold) quality of standard EBL based fabrication schemes. A sketch illustrating the fabrication process combining the two fabrication techniques is depicted in Figure 1. A detailed description of the individual process steps can be found in the Experimental sections.
section. Altogether this process results in designed gold nanostructures on arbitrary 3D dielectric templates.

Figure 2 displays a variety of 3D gold nanostructures designed to demonstrate the feasibility of this hybrid approach. In Figure 2a we show a proof-of-principle structure consisting of 20 nm thick gold lines processed on top of a DLW photoresist structure with a height of approximately 500 nm. By tilting the gold lines by 45 degrees with respect to the underlying DLW photoresist lines, as best seen in the inset, we also demonstrate a simple way of breaking the mirror symmetry, thus rendering the resulting gold structure chiral. Note that even steep elevations at the edges of the DLW photoresist structure can be covered by connected gold patterns. This can also be seen in the upright, omega-shaped structure shown in Figure 2b processed by our approach in combination with a precision alignment procedure. Again connected gold wires are formed despite a slight undercut present in the cross-sectional shape of DLW photoresist line. Figure 2c shows a geometry inspired by tapered Yagi-Uda nanoantennas,[25–27] demonstrating the possibility of defining finite curved 3D nanoantenna structures with our method. Taking this idea one step further, an array of curved 3D gap nanoantennas is displayed in Figure 2d. These two example nanoantenna structures are pointing towards the possibility to form integrated nanoantenna architectures, aiming at efficiently coupling nanoantenna tailored radiation from quantum emitters directly into optical waveguides defined via DLW, and making use of unidirectional emission using Yagi-Uda nanoantennas and/or of a strong emission enhancement by placing quantum emitters inside a nanoantenna’s feedgap. Furthermore such curved nanoantennas shown in Figure 2c,d may also be used to exploit magnetic coupling effects between the single elements of the arrayed nanoantennas. Notably, our approach indeed allows for assessing the 2D design freedom and nanoscopic feature sizes of planar EBL, as can be seen from the gap nanoantenna structure shown in Figure 2d, featuring a centre-to-centre distance between adjacent gap nanoantennas of 200 nm, their width measuring 60 ± 5 nm, and the gap size being 100 ± 15 nm.

In order to assess the optical properties of gold nanostructures fabricated along these lines we have designed and experimentally realized a 3D optical test structure consisting of arrays of upright-standing split-ring resonators (uSRRs), which can be used as fundamental building blocks for isotropic photonic metamaterials [4,15] or for metamaterial integration with optical waveguides.[28] This magnetic metamaterial is depicted in Figure 2e, where the inset shows a magnified top view. The diameter of the DLW photoresist line is 400 ± 5 nm, the
Two distinct resonances can be clearly identified for perpendicular polarization (red line). These correspond to excitation of the fundamental and the 1st order magnetic resonances of the uSRRs. For parallel polarization (blue line), on the other hand, no resonant feature is present in the displayed spectral range. Again, this is according to our expectations, since in contrast to planar SRRs the fundamental electric resonance of the uSRRs cannot be excited in this configuration.

In order to compare our experimental findings with theory we have performed finite-difference frequency-domain simulations using CST Microwave Studio and the geometry visualized in Figure 3b. Details of the implementation can be found in the Experimental section. In these calculations we have artificially reduced the centre-to-centre distance between neighbouring photoresist lines to 600 nm, as visualized by the purple box in Figure 3b, in order to shift the Wood-anomalies out of the wavelength range of interest, and to avoid the theoretical spectra to be disturbed by their occurrence. Additional calculations featuring a photoresist line spacing of 2 μm can be found in the Supporting Material. In experiments, Wood-anomalies are smoothed out by continuous angle-averaging, the spectral resolution of the setup, and sample imperfections. The results

centre-to-centre distance between neighboring photoresist lines is 2 μm, and their height derived from oblique-incidence SEM images is 280 ± 50 nm. The evaporated gold thickness is 50 nm. The centre-to-centre distance between adjacent uSRRs is 200 nm, the width of each written gold line measures 65 ± 5 nm, and their projected length is 375 ± 15 nm. The alignment error is approximately 20 nm, leading to a slight asymmetry of the experimental uSRRs. A close up SEM image of the fabricated structure and a ray tracing image visualizing the idealized geometry with experimental structure parameters are depicted in Figure 3a,b, respectively.

In order to evaluate the optical quality of the uSRR arrays, we have measured the linear-optical transmittance spectra in the spectral region from 0.8–3 μm. The measured transmittance spectra for the fabricated structure are depicted in Figure 3c. The incident light is linearly polarized with the electric field oriented either parallel (blue line) or perpendicular (red line) to the DLW photoresist lines, as indicated in the inset. In order to cover a sufficiently large spectral range we have performed two independent measurements, using both a home-built white-light spectroscopy setup connected to an optical spectrum analyzer (OSA) sensitive in the near-visible spectral range (800–1600 nm), and a Fourier-transform IR (FTIR) spectrometer (Bruker Tensor) connected to a Bruker Hyperion 1000 IR microscope (NA 0.5 Cassegrain objectives) for measurements at longer wavelengths (1450–3000 nm). Two distinct resonances can be clearly identified for perpendicular polarization (red line). These correspond to excitation of the fundamental and the 1st order magnetic resonances of the uSRRs,[24] For parallel polarization (blue line), on the other hand, no resonant feature is present in the displayed spectral range. Again, this is according to our expectations, since in contrast to planar SRRs the fundamental electric resonance of the uSRRs cannot be excited in this configuration.

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of our calculations are shown in Figure 3d. They show a very good overall agreement with the experimental spectra and allow us to identify the measured resonance at around 1.8 μm with the fundamental magnetic resonance, and the resonance below 1 μm with the 1st order magnetic resonance of the uSRR. Note however, that a quantitative comparison of resonance strength with experimental data is not possible, as the uSRR density assumed in theory is significantly higher than in the experiment, resulting in more pronounced resonances. Calculated mode-profiles (magnetic energy density in a 2D plane cutting through an uSRR) for the two modes are shown in the insets of Figure 3d, clearly revealing the magnetic character of the excited resonances.

In conclusion we have suggested and demonstrated a novel hybrid fabrication approach combining the advantages of DLW and EBL based micro- and nanofabrication schemes, and thereby allowing for the fabrication of designed 3D metal nanostructures for advanced plasmonic applications in the near-visible and NIR spectral range. The optical properties of fabricated uSRR structures are in good agreement with theory, confirming the high optical quality of structures fabricated along these lines and indicating that a magnetic response is achieved in these structures owing to their extension into the third dimension. We believe that our work offers a practical, easy to implement, and versatile way of pushing the operation frequencies of 3D metal nanostructures to the NIR and visible spectral range and that it will stimulate further activities to provide blueprints for 3D metamaterial and nanoantenna geometries that are compatible with our approach, paving the way to unlock the huge technological potential offered by 3D chiral metamaterials, 3D nanoantennas, and waveguide-integrated nanoplasmonics, to name just a few.

Experimental Section

Three-Dimensional Metal Nanostructure Fabrication: First DLW is performed on standard glass cover slides in the negative-tone photoresist IP-L from Nanoscope. Cross-shaped alignment markers are included in the writing process at the corners of each structured field. For development, the exposed sample is inserted into 2-propanol for 20 minutes before blow-drying it with a flow of nitrogen. The photoresist structures are then sputter-coated with 7 nm of Indium-Tin-Oxide (ITO) in order to prevent charge accumulation at the surface of the template during EBL. Because the sputtered ITO is already transparent in the optical spectral range after deposition and does not require additional annealing at elevated temperatures, we avoid damage to the photoresist structures and preserve the shape of the 3D template. In the next step, the ITO-covered photoresist structures are spin-coated with PMMA (Microchem PMMA A4). In order to obtain a sufficiently thick layer we have spin-coated a first layer of PMMA (3000 rpm, 90 s), performed a 10 min soft-bake in a convection oven at 170 °C, and then spin-coated a second identical layer on top of the first one, followed by a second soft-bake at 170 °C for 30 min. This results in a final PMMA thickness of 385 nm measured with a Tencor alpha-step 200. Next, the PMMA is exposed via EBL where the cross-shaped markers defined during DLW are used to precisely align the EBL pattern with respect to the existing DLW photoresist structure. After PMMA development a 50 nm thick gold film is deposited onto the sample surface by electron-beam evaporation and a standard lift-off procedure in hot acetone is performed.

Numerical Calculations: For CST Microwave Studio finite-difference frequency-domain simulations we have used experimental structure parameters taken from SEM images and an adaptive mesh. The refractive index of the glass substrate and the DLW photoresist lines was taken as 1.5. For simplicity we have neglected the thin ITO layer. The gold was modeled as a Drude metal with a plasma frequency of $1.33 \times 10^{16}$ rad/s and a collision frequency of $1.13 \times 10^{14}$ s$^{-1}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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