Subproject A1.5

Photonic Metamaterials

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On average, this corresponds to 1.5 full-time-equivalent scientist positions funded by the CFN.

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Introduction and Summary

Broadly speaking, photonic crystals as well as photonic metamaterials can be viewed as artificial optical materials exhibiting properties that simply do not occur in any known natural material. Hence, these man-made materials allow for performing novel optical functions. In subproject A1.5, which started in the year 2005 based on our early paper on magnetic metamaterials operating at around 3-µm wavelength published in *Science* in 2004, the focus lies on periodic structures for which the period or lattice constant is smaller (ideally much smaller) than the wavelength of light. Thus, for optical or even for visible frequencies, the required feature sizes are on the nanometer scale.

In the timeframe 2006-2010, subproject A1.5 has delivered results that have outperformed our most optimistic hopes. For example, our femtosecond interferometric experiment giving direct evidence for negative phase (and group) velocity of light in a double-fishnet-type metamaterial operating at 1.5-µm wavelength was published in *Science* in 2006 [A1.5:4]. In the same year and again in *Science*, we reported on unusual second-harmonic generation from magnetic split-ring resonator arrays at 1.5-µm wavelength [A1.5:7]. Early 2007, we reported in *Science* on the same behavior at visible wavelengths [A1.5:11,13].

However, all of these structures made by electron-beam lithography within the CFN were not really "materials" yet, but rather monolayers of meta-atoms. Moreover, certain phenomena such as, e.g., chirality, exclusively exist in three dimensions. Inspired by the three-dimensional direct-laser-writing (DLW) technology developed in the "neighboring" CFN subproject A1.4 since the beginning of the CFN, subproject A1.5 started an effort towards truly three-dimensional photonic metamaterials. A first success based on DLW and subsequent chemical-vapor deposition of silver was published in 2008 in *Nature Materials* [A1.5:21]. This technology was later outperformed by our work on combining DLW with gold electroplating, published in *Science* in 2009 [A1.5:31]. The latter chiral structures can serve as compact and broadband (more than one octave) circular polarizer – a nontrivial function that represents an early "real-world" application of photonic metamaterials.

On this basis, subproject A1.5 started to go well beyond its original plans and dreams by investigating transformation optics in three dimensions. Transformation optics, driven by early ideas of Ulf Leonhardt, John B. Pendry, and David R. Smith, is based on tailored spatially inhomogeneous metamaterials. Invisibility cloaking can be viewed as a benchmark example for the far-reaching concepts of transformation optics. In 2010, we published our experimental results on the so-called carpet cloak in *Science* [A1.5:38] – the first invisibility cloak in three dimensions at any frequency. This result could be translated even to visible frequencies later in 2010 (in preparation).

- Altogether, in the timeframe 2006-2010, subproject A1.5 has delivered 48 publications, among which are 6 articles in *Science*, 3 articles in the *Nature* group, 12 in *Opt. Lett.*, 12 in *Opt. Express*, one 100-page review in *Phys. Rep.* [A1.4:9], coauthored by CFN member Kurt Busch, and one recent review article in *Physics Today* [A1.5:43].
- Since 2006, subproject A1.5 has led to 88 invited talks at international conferences, including 15 plenary talks and 4 tutorials.

- In 2006, Martin Wegener was awarded with the Carl Zeiss Award (jointly with Kurt Busch) for work on photonic crystals and photonic metamaterials in CFN project A1.
- In 2007, Stefan Linden was awarded with the DFG Heinz-Maier-Leibnitz Prize for his work on photonic metamaterials in subproject A1.5.
- In 2008, Martin Wegener became Fellow of the Optical Society of America (OSA) for "… his seminal experimental contributions to the fields of three-dimensional photonic crystals and metamaterials and for his service for OSA" in CFN project A1.
- In 2008, Gunnar Dolling obtained the Junior Nanoscience Award of the BMBF-funded "Arbeitsgemeinschaft der Nanotechnologie-Kompetenzzentren in Deutschland“" for his PhD thesis in subproject A1.5.
- In 2010, Stefan Linden was awarded with the Gaede Prize of the German Vacuum Society for his work on photonic metamaterials in subproject A1.5.
- In 2010, Stefan Linden accepted the offer for a professorial position at Universität Bonn.

1. Photonic Metamaterials by Electron-Beam Lithography

Following our early work on magnetic photonic metamaterials made by electron-beam lithography [A1.5:1,3], the next challenge was to achieve negative phase velocities of light based thereupon. Aiming at a "smoking-gun" demonstration, we performed interferometric optical experiments on double-fishnet-type negative-index structures. Figure 1 gives an example of measured data.

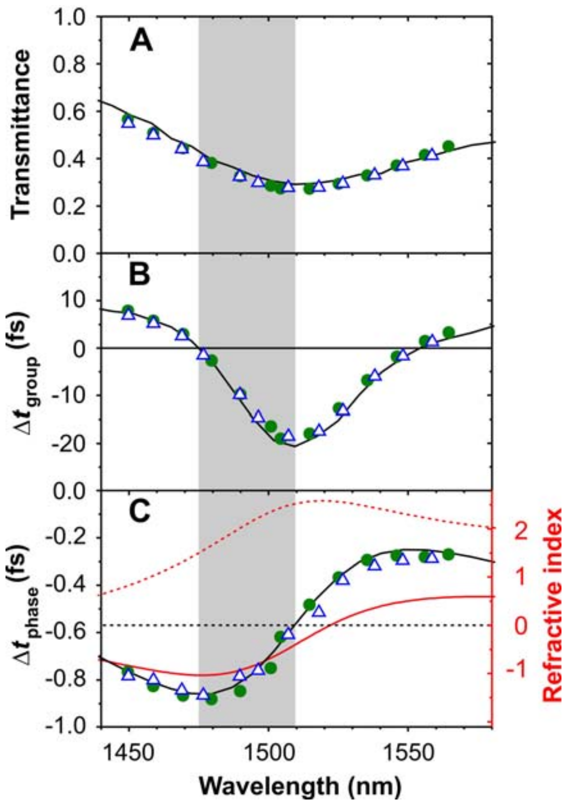

Fig.1: Results of femtosecond interferometric time-of-flight experiments on a gold-based double-fishnet negative-index photonic metamaterial operating at telecom wavelengths. Taken from Ref.[A1.5:4].

Several theoretical publications had assumed that the group velocity would be positive, hence opposite to the negative phase velocity of light. To address this aspect, we have analyzed the center of gravity (or the maxima) of the measured interferograms with Gaussian envelope. It immediately turned out that the group velocity can be negative as well – again in excellent agreement with theory. One simply must not make the erroneous assumption that the group velocity vector and the Poynting vector are parallel. Phase velocity and Poynting vector are indeed anti-parallel. Yet, the direction (or sign) of the group velocity depends on the dispersion. In the regime of anomalous dispersion, the group velocity can be negative even for positive phase velocity [A1.5:4].

Following causality, leading to the Kramers-Kronig relations, the dispersion of the real part of the refractive index inherently and unavoidably leads to a finite imaginary part as well. Undesired losses result. These losses are immediately obvious from Fig.1(a) and from the reduction of the red interferogram amplitude with respect to the blue interferogram. From comparison with theory we know that the losses are not due to fabrication imperfections but rather inherited from the metal losses under these conditions.

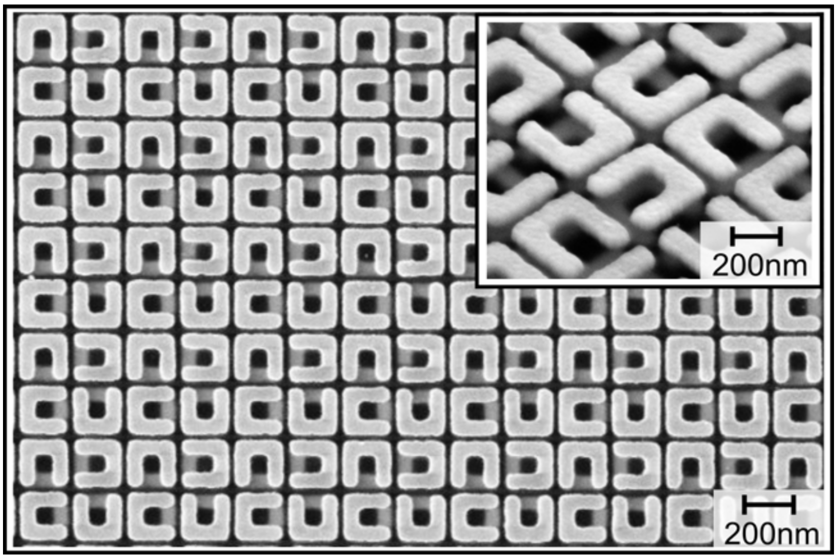

Fig.2: Top-view electron micrograph of a chiral photonic metamaterial composed of twisted gold split-ring resonators. The inset shows an oblique view. Taken from Ref.[A1.5:39].

Later in subproject A1.5, we fabricated lower-loss negative-index structures based on silver rather than gold [A1.5:5], the first negative-index structures operating in the visible [A1.5:11,13], as well as first structures composed of three functional layers [A1.5:15] rather than just a single one.

The field of metamaterials started with the idea that the metamaterial optical properties are solely determined by resonances of the individual building blocks and that interaction effects among them (leading to Bragg-type of resonances) are of minor importance. In contrast, our experiments have shown that interaction effects can be quite important. In our corresponding studies, we have followed three different approaches. First, angle-dependent spectroscopy can reveal dispersion effects that can be interpreted as being due to magnetization waves [A1.5:6,10,27,33,44] – the classical counterpart of magnons in solids. To the best of our knowledge, subproject A1.5 was first to observe these effects at optical frequencies. Second, comparison of experiments on arrays and on *individual* meta-atoms can give important insights [A1.5:22,36]. At this point, the cooperation with Kurt Busch's group within the CFN was again crucial. Third, near-field (as opposed to far-field) optical experiments can directly visualize the local electromagnetic field distributions [A1.5:40,44], including the local phase fronts near negative-index photonic metamaterials [A1.5:40].

While negative phase velocities of light have excited researchers and laymen alike, other functions of photonic metamaterials may eventually prove to be more useful in real-world applications. Nonlinear optical properties, like, e.g., frequency conversion are an example, which was already mentioned by John Pendry and his group in their pioneering theoretical paper on the split-ring resonator in 1999 [1] (also see review [2]). In 2006, we published first experiments on second-harmonic generation from planar split-ring resonator arrays [A1.5:7]. Here, the nonlinearity stems from the metal itself – which we believed at the time would be a much simpler situation to study compared to adding other nonlinear materials into the metallic metamaterials. The opposite turned out to be true. Even after a series of papers exploring the intrinsic metal nonlinearity [A1.5:7,17,23] (partly in collaboration with Jerome Moloney's theory group, Tucson), its microscopic origin is still not fully clear. CFN member Kurt Busch's group is presently working on developing the theory, including bulk and selvedge contributions. We are additionally performing true nonlinear optical *spectroscopy* experiments to clarify. In contrast, adding the non-inversion-symmetric semiconductor GaAs as an additional optical nonlinearity to split-ring-resonator based metamaterials, has led to improved second-harmonic conversion efficiency and to excellent experiment-theory agreement [A1.5:30] right away.

Chirality also requires a pronounced magnetic response and can lead to functions like strong optical activity and strong circular dichroism. Corresponding structures composed of two functional layers have been fabricated by electron-beam lithography, followed by planarization, reactive-ion etching, and a second carefully aligned step of electron-beam lithography. In this fashion, we have successfully fabricated and characterized twisted-cross metamaterials [A1.5:16,32] and twisted split-ring-resonator photonic metamaterials [A1.5:39]. Refractive-index differences between the two opposite circular polarizations as large as Δn=2 have been achieved by us [A1.5:39]. This is the largest value obtained in this wavelength regime to date. An example of a corresponding electron micrograph is depicted in Fig.2. This work has been performed in collaboration with Costas Soukoulis' theory group (Iowa State).

Many of the above photonic metamaterials still suffer from excessive losses. An obvious approach to reduce losses is to introduce active gain materials into or close to the metamaterials. While many groups have simply added constant gain into their theoretical calculations, we have pointed out that actually self-consistent theoretical calculations are mandatory because stimulated emission efficiently depletes the gain once the gain exceeds the loss [A1.5:24,29]. The coupled system of an inverted gain resonance evanescently coupled to a plasmonic metamaterials resonance exhibits similarities with the spaser introduced by Mark Stockman [3] as well as the lasing spaser by Nikolay Zheludev [4] and is interesting in itself. Following along these lines, our experiments have succeeded in achieving at least partial loss compensation upon optical pumping of single InGaAs quantum wells with intense femtosecond optical pulses at low temperatures [A1.5:45]. The semiconductor wafers for these experiments were provided by Galina Khitrova's group (Tucson); their TEM characterization was performed in CFN member Dagmar Gerthen's group.

Finally, for many of the envisioned applications, one would like to be able to tune the metamaterial's resonances by an external stimulus, ideally by simply applying a bias voltage. To this end, subproject A1.5 has closely collaborated with subproject A1.6 headed by Jörg Weißmüller within the CFN. Using electrochemical means, we have achieved frequency modulation of split-ring-resonator resonances as large as 50 THz at a center frequency around 300 THz for voltages as low as about one Volt [A1.5:42]. In this approach, which is closely similar to a field-effect transistor, we simply modulate the metal's surface charge density via the electrolyte and subsequently change the effective thickness or plasma frequency of the metal (gold) electron gas, obviously leading to plasmonic resonance shifts. Again, theoretical support has been provided by Kurt Busch's group in CFN project A1. A side aspect of this research can also be used to reduce the losses of photonic metamaterials [A1.5:48].

2. Photonic Metamaterials by Direct Laser Writing

While several meta-atom layers can painfully be stacked using electron-beam lithography (see previous section), this approach does not allow for truly three-dimensional structures. Thus, around the year 2007, we have started an effort based on direct laser writing (DLW), which we have developed over the years in subproject A1.4 for dielectric photonic crystals (see report on subproject A1.4). However, to fabricate metallic metamaterials along these lines, some sort of metallization in three dimensions is obviously crucial. Thus, we started two independent efforts, one based on chemical vapor deposition of silver and another one based on gold electroplating.

Chemical vapor deposition (CVD) can be viewed as the three-dimensional counterpart of vacuum evaporation. While CVD of dielectrics is well established and often quite simple, deposition of smooth metal films is rather difficult. Based on work of two Diplom theses, we have built within subproject A1.5 a CVD apparatus for silver that works in between a purely static and a dynamic-flow mode. Along these lines, we were able to deposit reasonably high quality silver films of about 30-nm thickness on three-dimensional polymer templates made by DLW [A1.5:21].

This technology has allowed us to obtain magnetic resonances [A1.5:21] as well as negative-index metamaterials [A1.5:25]. In contrast to purely planar layers, however, three-dimensional structures can not necessarily be described adequately by electric permittivity and magnetic permeability only. Bianisotropy can play a significant role and has indeed played a substantial role in our experiments [A1.5:21,25,26,35]. Bianisotropy means that magnetic-dipole moments can be excited by the electric component of the electromagnetic light wave and that, vice versa, electric-dipole moments can be excited by the magnetic component of the electromagnetic light wave. Chiral metamaterials (see preceding section and also see below) are a subclass of bianisotropic metamaterials in that the induced moments are oriented along the direction of the respective exciting field component, whereas they can have any direction in the general bianisotropic case.

The second route that we have followed within subproject A1.5 is based on DLW and subsequent gold electroplating [A1.5:31]. Here, a thin transparent indium-tin-oxide (ITO) electrode is deposited onto the glass substrate prior to DLW. This ITO layer forms one electrode for the electrochemical deposition of gold in an aqueous electrolyte. This technology has been developed in collaboration with the group of Volker Saile from Mechanical Engineering within KIT. While it appears simple, and actually is simple as well as inexpensive, it has taken us quite some effort to identify the appropriate process parameters.

This work is presently being extended towards electrochemistry of dielectrics *and* metals, such that metal/dielectric heterostructures could be grown in polymer templates made by DLW. CuO and Cu are used as a first example because the electrode potential allows deciding, which of the two is being deposited. If successful, this avenue would obviously greatly increase the flexibility of the overall approach. Here, discussions with CFN member Rolf Schuster from research area C have been very helpful.

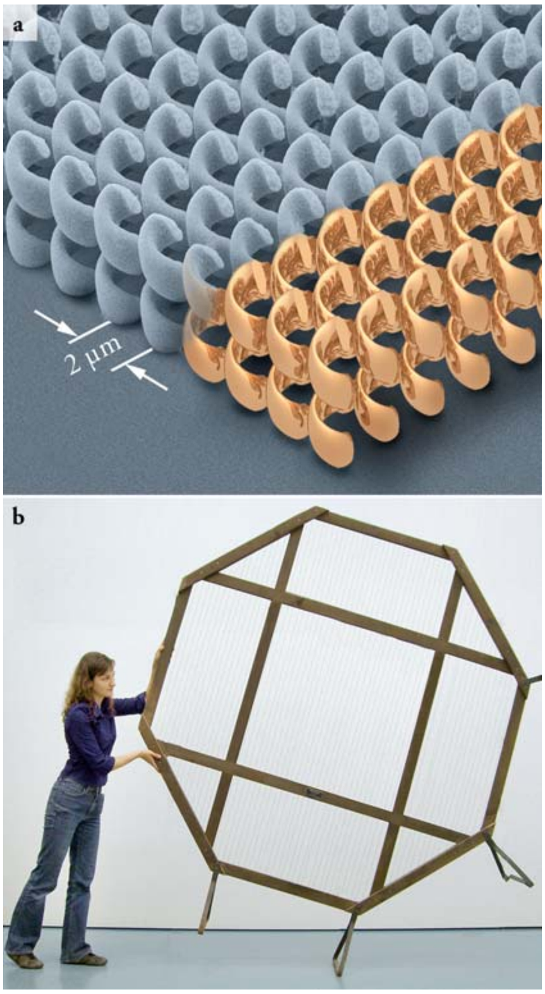

Fig.3: Circular and linear polarizers. (a) Gold-helix metamaterial composed of submicron gold helices arranged into a uniaxial square lattice. The measured oblique-view electron micrograph is shown in the background, the structures used for the theoretical calculations in the foreground. This structure can be applied as a compact circular polarizer with more than one octave bandwidth (about 3.0 to 6.0 µm wave-length) and is the circular analogue of the good old wire-grid polarizer already used in Heinrich Hertz' pioneering experiments on electromagnetic waves in Karlsruhe in 1887 shown in (b). Taken from Refs.[A1.5:31,43].

The first published example [A1.5:31] of this technology is visualized in Fig.3. Here, we have written air helices into a positive-tone photoresist. The electroplating is followed by plasma etching of the polymer, leading to square arrays of three-dimensional gold helices. Interestingly, the electromagnetic interaction of the different helix pitches plays a crucial and beneficial role (also see discussion on interaction in the preceding section): This interaction lifts the degeneracy of the resonances and thus leads to the formation of bands of magnetization waves. The corresponding stop band in the transmittance spectrum for light propagating along the helix axes has an amazing bandwidth of about one octave. One circular polarization of light is correspondingly not transmitted, whereas the other one is almost completely transmitted. Thus, this device can be viewed as a circular polarizer. Light of any polarization impinging onto this circular polarizer leads to transmission of only one circular polarization of light. Importantly, the same task can *not* be achieved with a usual linear polarizer followed by a usual quarter-wave plate, because the quarter-wave plate turns into a half-wave plate upon changing the wavelength of light by a factor of two. Our demonstration [A1.5:31] has been for the wavelength interval 3-6 µm, where the "fingerprint" resonances of many chiral molecules are located in. The device concept is size-scalable to other wavelength regimes. The device performance can systematically be improved by going towards more than just two helix pitches [A1.5:37]. Structures with up to four pitches have been made within subproject A1.5 (unpublished). Presently, A1.5 work aiming at exploring other polarization geometries of metal-helix based photonic metamaterials is in progress.

3. Transformation Optics

So far, we have tacitly assumed that all meta-atoms of the structure are identical. Further design freedom arises for intentionally spatially inhomogeneous structures [5-8]. Suppose we want to force light to take certain predefined pathways. According to Fermat's principle in optics or the geodetic principle in General Relativity, any light ray takes the path from point A to point B that corresponds to the shortest (phase) propagation time. By tailoring the local phase velocity of light (via the local refractive index), we can minimize the time for selected pathways. The mathematics of transformation optics [5-8] provides us with an explicit construction principle. Transformation optics starts from a possible fictitious distortion of space (more generally of space-time) that corresponds to the desired pathways. Using a suitable mathematical transformation of the Maxwell equations, this distorted empty space ($\varepsilon = \mu = 1$) can be mapped onto a Cartesian coordinate system (as available in usual laboratories) filled with a special material following spatially varying electric permittivity and magnetic permeability tensors $\ddot{\varepsilon}(\vec{r}) = \ddot{\mu}(\vec{r})$. In other words, it is the optical path length that matters in Fermat's principle. For an infinitesimally small path element, the optical path is simply the product of the geometrical path length and the local refractive index $n(\vec{r})$. Thus, a change in geometrical path length can be mimicked by a change in refractive index. Finally, the condition $\ddot{\varepsilon}(\vec{r}) = \ddot{\mu}(\vec{r})$ guarantees that the wave impedance is globally equal to the vacuum impedance $Z_0 = \sqrt{\mu_0 / \varepsilon_0} = 376.7\Omega$, leading to vanishing reflections of light.

However, the profiles emerging from transformation optics often involve singularities and other aspects that are difficult to actually achieve in an experiment. The so-called carpet cloak introduced by Jensen Li and John Pendry in 2008 is a notable exception [9]. Its three-dimensional version is depicted in the top panel of Fig.4. Arbitrarily shaped objects can be hidden underneath the bump in a metallic carpet. To hide this bump, a graded-index profile is added on top that makes the metallic carpet appear flat, hence unsuspicious. In our 2010 experiments, this index profile has been mimicked by a three-dimensional polymer woodpile photonic crystal used in the long-wavelength (or effective-medium) limit. For example, a local volume filling fraction of 100% leads to the refractive index of the polymer (1.52 in our case), 0% volume filling fraction to the index of air, i.e., 1. After fabrication of this highly complex structure via DLW, the entire structure is coated with gold in a sputter chamber [A1.5:38].

An example from the optical characterization published in Ref.[A1.5:38] is shown in the bottom panel of Fig.4. The bump without cloak appears as a bright stripe in the dark-field microscopy image (left), whereas hardly anything remains visible for the structure including the cloak (right). These experimental results are very well reproduced by ray-tracing calculations including the complete microscope imaging process [A1.5:41]. Photorealistic images have previously been published by us as well [A1.5:34]. Truncated conformal maps allow for systematically improving the cloaking performance [A1.5:46]. Work on quantifying the cloaking performance by means of cross-correlation functions is in progress.

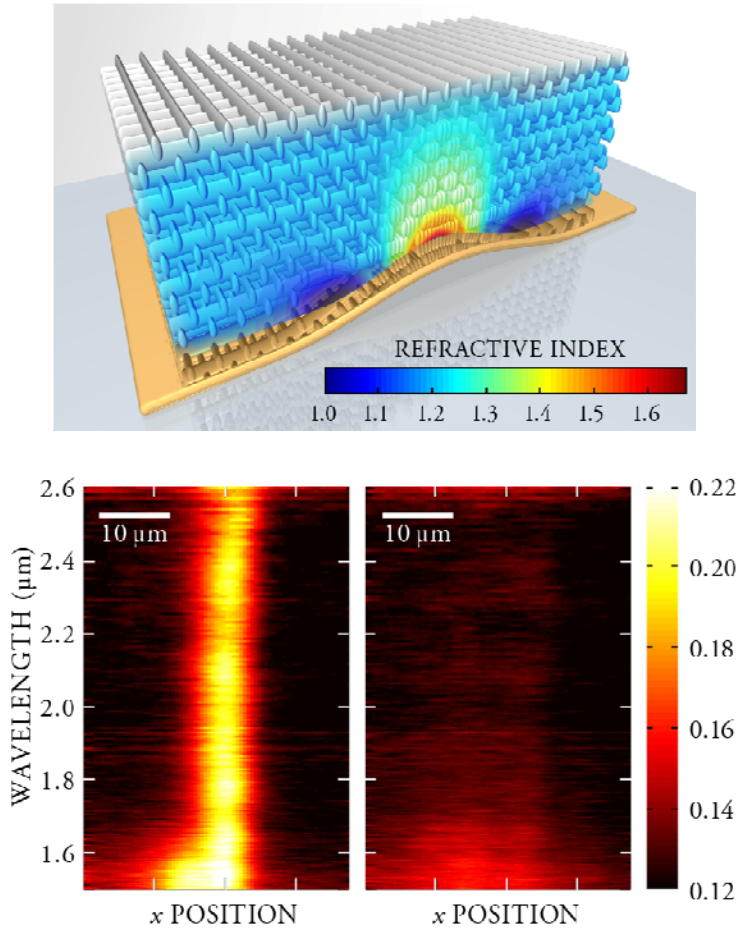

Fig.4: Scheme of a three-dimensional invisibility cloaking structures that has been fabricated within CFN subproject A1.5 using direct laser writing (top panel). The bottom panel exhibits the measured performance with a reference structure on the left and the cloak on the right. Taken from Refs.[A1.5:38,43].

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[9] J. Li and J.B. Pendry, *Phys. Rev. Lett.* **101**, 203901 (2008)

We also refer to the large number of references to the vast literature given in our own reviews in *Science* [A1.5:13] in 2007, in *Physics Reports* [A1.4:7] in 2007, in *Physics Today* [A1.5:43] in 2010, and in *Science* [A1.5:47] in 2010. Furthermore, the following review articles in the German popular-physics magazine *"Physik in Unserer Zeit"* have emerged from subproject A1.5

- G. Dolling, S. Linden, and M. Wegener, *Metamaterialien: Licht im Rückwärtsgang*, Phys. Unserer Zeit **37**, 157 (2006)
- G. Dolling, M. Wegener, and S. Linden, *Der falsche Knick im Licht*, Phys. Unserer Zeit **38**, 24 (2007)
- M. Wegener, *Zum 150. Geburtstag von Heinrich Hertz: Wenn Funken Wellen schlagen*, Phys. Unserer Zeit **38**, 149 (2007)
- J.C. Halimeh, T. Ergin, N. Stenger, and M. Wegener, *Transformationsoptik: Massgeschneiderter optischer Raum*, Phys. Unserer Zeit **41**, 170 (2010)
- N. Stenger, T. Ergin, and M. Wegener, *Dreidimensionale optische Tarnkappe realisiert*, Phys. Unserer Zeit **41**, 218 (2010)