Executive summary

Eight European universities, coordinated by EPFL, came together in NANOGOLD, an EU-funded project, in order to discover and achieve new metamaterials with properties never observed in nature and which are today belonging rather to the realm of science-fiction.

The goal was to develop future materials (bulk 3D optical metamaterials) which are at the heart of applications that promise to revolutionize various fields of science. A referential example is a material that is part of an imaging device that possesses a resolution which outperforms established microscopes by orders of magnitude. Alternatively, materials were developed that can conceal objects for an external observer and to let it be invisible. Or even further, materials were developed that absorb completely the light across a large spectral domain. The absorbed light in these materials is converted into heat, which can be used on the nanoscale in e.g. catalytic or thermo-photovoltaic applications. The novelty of our approach was to use methodologies of self-assembly to fabricate these metamaterials. This entailed the use of the materials as an ink which can be fabricated cheap, in large quantities, and which can be deposited on arbitrary objects.

The incredible material properties are obtained by incorporating small and resonant entities into a periodic or even amorphous nanoscopic structure. Under different options we identified metal nanoparticles, which are readily available as the most promising entities to achieve a significant interaction of light with matter. Unique to our approach, is the assembly of meta-atoms made from a large number of metallic nanoparticles with a well defined geometry to form the composite material. The nanoscopic structure allows these composites to behave as a homogeneous material with properties largely different from those observed in its constituents. The collective resonance of these nanoinclusions appears only when a critical number of resonant units are unified, in the same way that a single molecule of H_2O is not wet, but many of these molecules form water.

In this project, research followed an interdisciplinary approach and combined visionary inorganic chemistry, organic synthesis, macromolecular physics of electromagnetic resonance, and liquid-crystal technology. The organization of nanoparticles composing the metamaterials was obtained using the techniques of liquid-crystal molecules which are able to self-organize. The advantage of using this technology was that the structural parameters of the material could be controlled by external means, making the material properties adjustable according to various parameters such as temperature, electric field, or light for examples.

To obtain a regular structure of the metallic nanoparticles, they were directly introduced into an organic molecule containing mesogenic (liquid-crystalline) entities. The resulting hybrid molecules self-assemble via intermolecular interaction. After analysis of both the individual components – the hybrid molecules – and the material as a whole, theoretical simulation of the optical properties guided the researchers in the most effective direction in terms of material realization. This reverse-engineering approach helped researchers to understand how the materials properties could be modified and enhanced.

Applications for this research are still under discussion, but some immediate areas have already been identified. The main idea is to create devices that are transparent for certain wavelengths but not for others. This is already possible to do today, but requires the use of complicated multi-interference structures. In this project, the focus is on the development of an ink that could be applied to a surface and would allow to get these functionalities and to create particular effect in a single layer, as a magic paint.

Summary description of project context and objectives

The development of new metamaterials, materials with properties different from their constituents, arouses an immense interest both for the scientific community and the industry due to the high potential of new applications and the possible improvement of already existing applications.

The use of amorphous structures with structural dimensions much smaller than the wavelength of light that are fabricated by means of self-organization and bottom-up principles could help researchers to mitigate some problems that exist with conventional metamaterials that are fabricated by top-down methods. This area forms the primary research focus of the NANOGOLD project. The aim was to fabricate and apply innovative and novel bulk three dimensional metamaterials by relying on bottom-up methods. The key driver was to transfer material design know-how from chemistry laboratories to materials technology to create artificial electromagnetic materials.

In this project, the basic idea was to use electromagnetic resonances on different scales to achieve new electromagnetic properties, based on the use of small metallic nanoparticles introduced in clusters or in films to serve as three dimensional bulk metamaterials. The focus was on amorphous systems that have several levels of structures but no strict periodicity.

Various innovative techniques were used to obtain such bulk metamaterials. One technique is based on the preparation of nanoparticle – liquid crystal composite units, which yield materials where the resonant particles are in a liquid-crystalline state. By changing the structure of the organic liquid-crystalline part, the structure of the material and its (optical) properties can be tuned. Another strategy relies on the use of electrostatic forces between charged plasmonic particles and polyelectrolytes. Starting from a suitably chemically modified substrate (e.g. glass), the sample can be built up layer-by-layer. This allows the tuning of the distance and therefore the coupling between the resonant entities, which has a drastic effect on the electromagnetic properties of the material. This approach is very flexible. For example different types of nanoparticles can be used for the different layers and the distance between them can be controlled within nanometer precision. Moreover, the approach is not limited to planar substrates, but metallic nanoparticles could be equally deposited on small dielectric beads. This has been opening completely new approaches to fabricate meta-atoms that possess, e.g., a strong magnetic dipolar response. It constitutes therefore the base for any advanced metamaterial.

In this project, one novelty was the use of chemical synthesis of basic units, which carry a first level functionality, i.e. a resonance, and which are ready to be used as building blocks for bulk assemblies. The bulk assembly can be random, amorphous, or regular and will add a second level of functionality. In such a way combinations of different functionalities become possible and the material design is simplified. It only has to be stressed that all occurring lengths scales should be smaller than the wavelengths of light to avoid visibility by naked eye, i.e. the final materials should be perceived as being homogenous.

The very small structure scales are achieved by starting material built up with nanoparticles that are two orders of magnitude smaller than the wavelength of light. Often nanoparticles with size below 10 nm are used and assembled in clusters or layers. They form a unit cell that is often called meta-atom. The intra-cell structure (or organization of nanoparticles inside this unit cell) determines to a large extent the optical response. The better it is controlled, the more effective the response can be

shaped, but there is no absolute need for strict periodicity on this level, although it is recommended.

The unit cells will be forced to form structures that have typical distances and size features below the wavelengths of light to avoid visibility. Here an amorphous arrangement is highly desirable because of the homogenization aspects mentioned above: One would like to have a uniform matter that shows no directional dependence due to its internal structure. An amorphous nanostructured system is an ideal playground to achieve properties just like in glass, another amorphous solid. In the following the major streams of research are sketched.

Nanoparticle- liquid crystal composite units

One important strategy of the consortium was the development of materials where the resonant entity, i.e. a gold nanoparticle, is covalently linked to organic entities that tend to self-assemble. In this way, the organic and inorganic parts are combined at the molecular level. This prevents a phase separation often observed in composite materials. Within these units all the information necessary for self-assembly is contained. Within this project we also learned how the properties of the composite units affect the material structural properties.

Ensuring that the material's homogeneity is not disturbed by the nanoparticle is a real challenge. As the metallic nanoparticles are spheres of typically 3-5 nanometers diameter, the organic part of the molecule has to be relatively large to carry and wrap them. The resulting material often has features that are not favourable for technology processing (for instance, the viscosity is too high, or it needs relatively high processing temperatures). However, it is possible to tune the properties of the material by manipulating the molecules in various ways. Working with thermotropic systems, where you can influence physical parameters like viscosity or structure by changing the temperature, allows adjusting the properties of the material. The effects on nanoparticle resonance and structural interference are different. The nanoparticles' properties and the related resonance are stable but the surrounding morphology and the interference is changing. This offers the possibility to tune the material properties and to freeze the structure to conserve it.

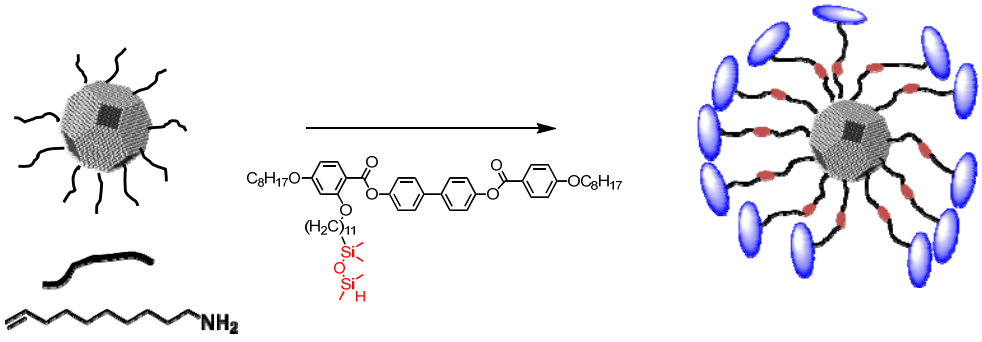

Figure 1: Schematic structure of the NPs prepared

Fabrication of complex structure containing dense nanoparticle arrangements (meta-atoms)

One of the main objectives of metamaterial fabrication is their effectiveness. This can be achieved by creating materials with high density of resonant entinties or metaatomes per volume. But this is areal challenges fot both physical chemistry of materials and

technology. If we consider first the realiztaion of matter containing high load of metallic nanoparticles it becomes clear that due to the high density of the metal part compared to the organic host (ratio about 1:10) an extreme load in weight has to realize. This is a research task in itself and it is fortunate that in recent years a lot of effort was put all around the world in realizing nanoparticle inks that contain more than 85% of weight of nanoparticles which corresponds to “only” 15% of volume filling fraction. The resulting distances of nanoparticles at such filling fractions allows already exploring coupling of resonances in nanoparticle clusters. This could be shown succeffully for a cluster matter of dense nanoparticle ink in constraint confinement and with that cluster matter metaatom was demonstrated.

In a different approach the number of resonant particles and their arrangement was considered. Because metallic nanoparticle have a rather large absorption way need to be find to dilute the system without loosing the specfifc response to minimize losses. One possibility is the use of core shell systems that contain nanoparticle deposited on a dielectric core. The effeiciency of such assemblies as metaatoms could be shown and for the first time a large number of such core shell metaatoms was realized as metaatom layer on a surface. A highly ranked achievement to obtain artificial materials based on designed metaatoms.

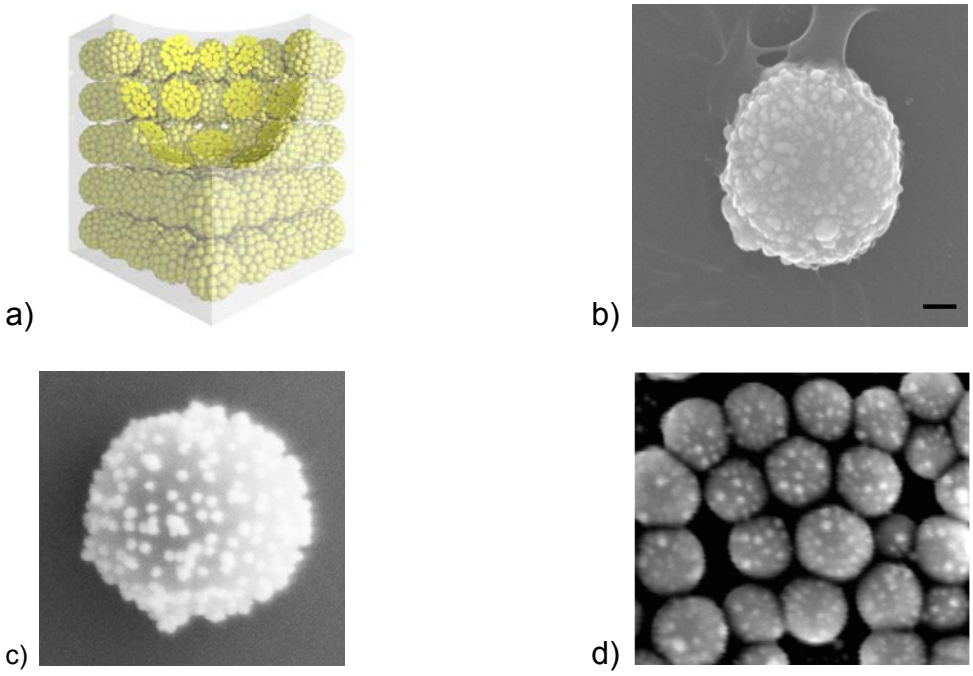

Figure 2: a) 3D orthorhombic metamaterial made of air cavities in silica containing clusters of gold NPs of 8nm radius. b) realization of dense nanoparticle cluster metaatom (Publication Jose OME 2012) c) SEM micrograph of core-shell gold nanoparticle cluster of 300 nm diameter with metallic nanoparticles of 20 nm in size, d) surface with a dense layer of metaatoms realized as core shell systems.

Layer-by-layer fabrication of metamaterial

Particles or meta-atoms arranged in layers lead to interesting electromagnetic properties if geometrical parameters can be varied over a wide range. A concept based on spin coating polymer films and nanoparticle solutions provides the possibility to vary density of particles and distances between the nanoparticle rich films as shown in Figure 3. Recipes to achieve dense particles or clusters (meta-atoms) assemblies in

multi-layers have been developed within this project. The advantage of such a more conventional technique is its immediate availability. Combination of multilayer and single layer interference with nanoparticle cluster matter was proven to be a convincing concept to realize highly environmental sensitive films. We have chosen fabrication methods that allow increasing the density of metallic entities inside the composite to its extremes – highly packed nanoparticles and no particles at all in well separated domains. The variation of parameters allows one obtaining optical properties not found in nature before.

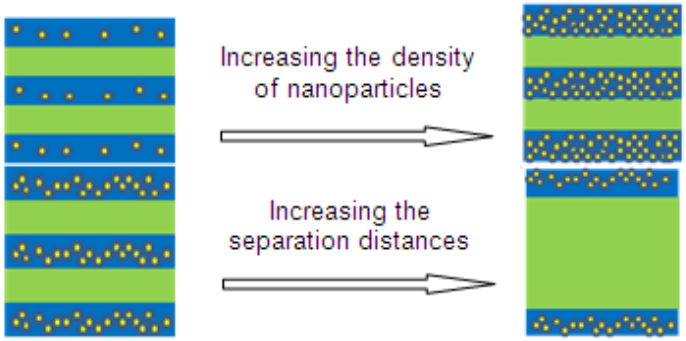

Figure 3: Schematic presentation of multilayer design where nanoparticlelayers and organic optical transparent materials for a amorphous cluster matter with specific optical properties. Density, distance, number of layers and kind of particles can be changed to adapt for best performance.

Besides spin coating the self-assembly of particles was achieved through layer-by-layer processing making use of the electrostatic interactions between polyelectrolytes and nanoparticles. Such preparation is very robust and can be automated using standard dip-coating equipment. Also, the constituents, polyelectrolytes and charged nanoparticles, are commercially available or can readily be prepared. The interesting optical properties of these systems arise through the spatial arrangement of the metallic nanoparticles within the polyelectrolyte host. Importantly, the arrangement does not need to be fully ordered to achieve most of the desired properties. The method is highly flexible and accurate positioning of the nanoparticle layers is possible within the nanometer range. These two attributes allow one to obtain optical materials by design. Macroscopic optical properties can be tuned at will by changing nanoscopic properties of the layer system such as the material, size, shape and density of the nanoparticles within one layer, the distance between the layers and the number of nanoparticle layers. In such a complex system the design and the optimization of the material properties has to be guided by simulations that can predict macroscopic (effective) properties based on the geometry of the sample, i.e. the arrangement of the nanoparticles. The layer-by-layer structures prepared in the project do not only have interesting properties itself but they can also alter the properties of molecules interacting with them. For example the fluorescence of molecules within such structures can be enhanced and the scattering of light by molecules can drastically be increased. The latter is interesting for sensing applications.

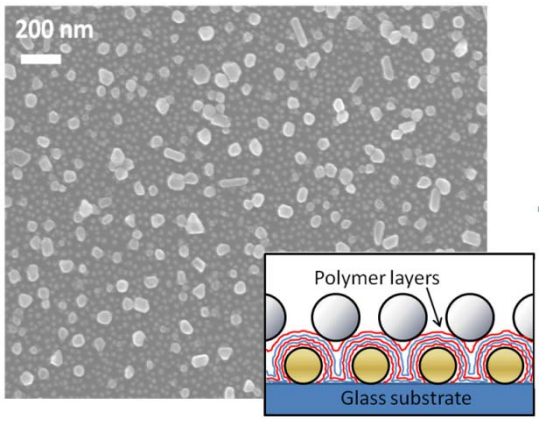

Figure 4: SEM image showing and schematic of an array of gold nanoparticles (~ 18 nm diameter) and an array of silver nanoparticles (~ 43 nm diameter) separated by 7 polyelectrolyte layers.

Description of main S&T results

The sections below describe the main scientific and technical results of the NANOGOLD project per Work Package (WP). Each section starts with a summary of results obtained in the corresponding WP and followed by the list of related scientific publications with keywords and abstract.

1.1. WP1 - Chemistry of self-organizing composite building blocks

The nanomaterials envisaged in the project NANOGOLD are a very specific set of materials which combine properties typically associated with gold nanoparticles such as plasmon resonances with properties of typically connected with organic low molar mass liquid crystal materials or LC polymers. This involves self organisation such as 1D, 2D or 3D self assembly across length scales, reaching from the nanometric to the macroscopic (eg. the length scale of an organized film 100nm thick film over several mm2 in an optical test device). Associated materials properties such as a control of the viscosity of the materials as well as the temperatures at which the 1D, 2D or 3D self assembly can be dialed in are to be designed in. From the starting point of spherical NPs a number of goals were to be achieved.

The starting point was the preparation the LC-NPs on a technical scale, based on the molecular architecture of the at outset best materials. This involved a subset of a target: namely finding a upscaling route for thiol based LC materials with LC properties at room temperature, upscaling of the Au NPs synthesis and the combination of both sets of materials in exchange reactions. This was achieved. Thiol based LC materials were prepared on the tens of gram scale and Au NPs functionalized with LC groups were prepared in subgram batches.

Based on this initial set materials the size of the NPs was systematically increased from 1.5 nm diameter to 3.5 nm diameter and later to 5nm diameter using thiol terminated capping agents. Whereas in the small NPS no plasmon resonance could be observed, this could be detected in the larger materials. The self-assembly properties were modulated by varying the length of the hydrocarbon chain between hexyl and dodececyl chains and by a variation of the structure of the LC group, though in this subset of studies the overall geometry, lateral linkage of a linear calamitic mesogen was maintained. Structural parameters which were varied were the length of the linkage group to the NPs, the length of the aromatic core and the ratio of linear hydrocarbon to LC groups linked to the NPs. A further parameter varied, was the polydispersity of the NPs. It was detected that more monodisperse NPs exhibit enhanced 2D and 3D self assembly properties. Generally speaking, the absence of co-ligands or long dodecyl linear co-ligands resulted in 3D self organization of NPs, shorter co-ligands favour formation of Au NP chains in 2D arrays, with lattice type and distance of the NPs controlled by type and number of LC groups present. For the investigation of the organisation of the organic groups on the NP surfaces partly deuterated surfaces nano-compositions were synthesized for temperature dependent neutron scattering experiments.

In order to address the issue of increased viscosity of larger NPs, a completely novel architecture of advanced NPs were designed ranging in size range from 6-11nm capped via amine terminated co-ligands. In order to assure low viscosity, high stability and control over self-assembly properties, a low glass temperature spacer involving siloxane groups was introduced via a hydrosylation positioned between the NPS and

the LC groups, achieving the goal of Au NPs with low viscosity, LC behaviour at room temperature and plasmonic responses.

For the exploration of chiral superstructures Au NPs were functionalized with newly designed cholesteryl based mesogens, using thus a sustainable natural product, were used connected either terminally or laterally to the NPS, resulting in LC behaviour at room temperature with the formation of chiral phases with 2D superstructure. In order to enhance the chiral properties novel ligands based on the bisnaphthol unit were designed and connected to LC groups resulting to very highly twisted chiral nematic LC phase formation. Attachment to au NPs resulted in novel high chirality LC NPs.

Chiral nematic organo-siloxane oligopodes based on an axially chiral binaphthalene core. The synthesis of a novel class of organosiloxane oligopodes, based on an axially chiral binaphthalene core is described and their mesogenic properties are fully characterised.

C. Schubert, M.G. Tamba, G.H. Mehl, *Chem Commun.* 48, 6851-6853, (2012).

Design, Synthesis, and Characterization of Mesogenic Amine-Capped Nematic Gold Nanoparticles with Surface-Enhanced Plasmonic Resonances. The use of the liquid-crystalline state to control the assembly of large (>5 nm) gold nanoparticles (NPs) is of considerable interest because of the promise of novel metamaterial properties of such systems. Here we report on a new approach for the preparation of large nematic gold NPs using a bifunctional capping agent that enables control over the particle size and serves as a linkage for subsequent functionalization with mesogenic groups. Properties of the NPs were characterized by HRTEM, NMR, DSC, TGA, UV/vis, OPM, and XRD studies. The results confirmed the formation of a stable nematic mesophase above 37.5 °C for NPs in the 6−11 nm size range.

C.H. Yu, C.P.J. Shchubert, C. Welch, B.J. Tang, M.-G. Tamba, and G.H. Mehl, *J. Am. Chem. Soc.*, 134, 5076-5079 (2012).

Control of anisotropic self-assembly of gold nanoparticles coated with mesogens. The self-assembly was investigated of a series of gold nanoparticles (GNP) that were covered with laterally attached mesogenic molecules (ligands) and different amounts of alkylthiols (co-ligands). The presence of mesogens induces long-range ordered packing of GNPs. Here we report three different ordered liquid crystalline phases built around the GNPs, two of which have not been observed previously in thermotropic liquid crystals. These are the 3D simple hexagonal packing and the facecentred cubic (FCC) packing of spheres, i.e. GNPs in this case. It has been found that the volume fraction of co-ligands in such systems is critical for the anisotropy of the self-assembly of GNPs; either too small or too large a co-ligand volume fraction causes the formation of one of the two nearly or fully isotropic packing types mentioned above. In these two structures the rod-like mesogens have no preferred orientation. At intermediate co-ligand fractions highly anisotropic strings of GNPs are obtained, packed in a 2D hexagonal lattice, with the mesogens surrounding the strings and lying parallel to their axis. […]. The results help us to understand and control the way organic molecules affect the organization of nanoparticles, and facilitate the design of new hybrid materials through self-assembly.

X. Mang, XB Zeng, B. Tang, F. Liu, G. Ungar, R. Zhang, L. Cseh, GH Mehl, *J. Mater. Chem.*, 22, 11101-11106 (2012).

One-Step Synthesis and Self-Assembly of Metal Oxide Nanoparticles into 3D Superlattices. A simple one-pot approach based on the "benzyl alcohol route" is introduced for the fabrication of highly ordered supercrystals composed of highly uniform 3–4 nm zirconia and rare-earth stabilized zirconia nanoparticles. The as-fabricated supercrystals reach sizes larger than 10 μm and present well-defined 3D morphologies such as flower-like, rhombic dodecahedron, and bipyramids. This system is unique in that the supercrystals are formed in one-step directly in the reaction medium where the nanoparticles are synthesized. The uniformity in nanocrystal shape and size is attributed to the in situ formation of benzoate species that directs the nanoparticle growth and assembly. The low colloidal stabilization of the benzoate-capped nanoparticles in benzyl alcohol promotes the formation of supercrystals in solution by π–π interaction between the in situ formed benzoate ligands attached to neighboring particles. By varying the reaction temperature and the nature of the doping the way the nanobulding blocks assemble in the supercrystals could be controlled. Standard FCC superlattice packings were found together with more unusual ones with P6/mmm and R3̄m symmetries. Similar to the case of spherical gold nanoparticles forced by the rod-like ligands of positive anisotropy to form anisotropic superlattices, so the discotic benzoate capping molecules created in-situ, are believed to form long-range orientational order causing anisotropic growth of nanocrystals with an isotropic (cubic) internal lattice.

A. Pucci, M.-G. Willinger, F. Liu, X.B. Zeng, V. Rebuttini, G. Clavel, X. Bai, G. Ungar, N. Pinna, *ACS Nano*, 6, 4382–4391 (2012).

GISAXS in the study of supramolecular and hybrid liquid crystals. The use of grazing incidence small and intermediate angle X-ray scattering in the study of structure and alignment of thermotropic liquid crystals is illustrated on selected examples. These include columnar LC phases of a star-shaped mesogen, several honeycomb phases of T-shaped and X-shaped bolaamphiphilic LCs, and gold nanoparticles coated with mesogenic ligands. Sharp Bragg reflections from systems with 2-d and 3-d periodicities are obtained through annealing. Due to nearly perfect surface alignment in most cases, indexing of complex diffraction patterns is facilitated. Honeycomb cells with deformed hexagonal cross-sections, as well as kagome lattice, are shown. The tilt of the reciprocal lattice is shown to help establish the correct structure in the case of the stretched hexagonal honeycombs and the rhombohedral arrays of ordered strings of gold nanoparticles.

G Ungar, F Liu, X B Zeng, B Glettner, M Prehm, R Kieffer and C Tschierske, *J. Phys.: Conf. Ser.,* 247, 012032 (2010).

1.2. WP2 – Chemistry and Physics of macromolecular metal composites

Nanostructured materials were prepared following several different bottom-up strategies. One mayor strategy focussed on the preparation of nanoparticle – mesogene entities that exhibit some liquid-crystalline behaviour. Other strategies were based on the use of preformed particles that were incorporated into some templates or on the systematic build-up of structures using structure directing agents or processes. In particular, the following achievements are reported:

- *Liquid crystalline metal nanoparticles:* Mesogenes were synthesized and covalently bound to gold nanoparticles. The mesogenes were also designed to yield low viscosity of the resulting nanogold composite in order to help organisation. Chiral

mesogenes were also synthesized with high helical twisting power. Relatively large gold nanoparticles covered by mesogenes showing liquid-crystalline behaviour could be prepared. The particles were large enough to show a clear plasmon resonance. The obtained liquid-crystalline structures were determined by GISAXS measurements. The samples showed a polarization-dependent shift of the plasmon resonance which represents the first evidence of a self-organizing material with electromagnetic plasmonic coupling.

- *Layer-by-layer deposition of nanoparticles:* Charge-driven layer-by-layer deposition was used to prepare monolayers, bilayers and multilayers of nanoparticles. Multilayers of gold nanoparticles with different interparticle distances showed very intense colours and the absorption spectra revealed complex coupling between nanoparticles in the different layers. Nanorods were also assembled into layers and anisotropic Au – Ag bilayers revealed dark modes as expected for coupling within asymmetric dimers. Very high density and ordered gold nanoparticle layers were prepared by a thiol wash procedure. The layer-by-layer deposition method was also performed on soft PDMS structures and stretching lead to diffraction gratings. Layered structures were also prepared by spincoating technology.
- *Layer-by-layer growth on structured surfaces:* Using lithographic methods substrates were structured and by using appropriate surface chemistry these structures were transferred to the layer-by-layer growth mediated by polyelectrolytes. In this way selected areas of the substrate could be covered by nanoparticles, whereas other areas were completely nanoparticle-free. Diffraction gratings could be prepared in this way.
- *Core-shell particles*. Silica beads were successfully coated with gold and silver nanoparticles to form core-shell structures. The optical response of these structures is dominated by a magnetic dipole as revealed by simulations of the corresponding structures. These structures also showed scattering properties which may indicate cloaking of the bead.
- *Nanoparticle – silica multilayers*: Layered structures were successively grown by depositing gold nanoparticles on a glass substrate followed by the growth of a thin silica layer on top. By repeating the process multilayers of gold nanoparticles separated by a thin layer of silica could be grown. The extinction spectra reveal coupling between the particles within the porous layer.
- *Spherical silver nanoparticle clusters by oil-in-water emulsion*. Silver nanoparticle droplets were formed in an oil-in-water emulsion. The samples had different colours for different cluster sizes. Their optical properties showed a broad red-shifted resonance possibly associated with magnetic activity.

For many of the described structures simulations of the respective nanoparticle assemblies (dimers, multi-layers, core-shell clusters and clusters) shed light onto the coupling mechanisms and in some cases effective optical properties could be extracted.

Plasmonic nanoparticles assemblies: preparation, structural, and optical properties. Self-assembly techniques are used to build complex amorphous structures from plasmonic particles. The assembly makes use of surface chemistry and intermolecular interactions between surfaces, surfactants, polymers and particles. The resulting two- or three-dimensional structures have optical properties that derive from the coupling between particles. A high control of the structural parameters on the nanometer scale can easily be achieved. In contrast to top-down techniques relatively large areas can be

prepared in a versatile manner thus paving the way to applications as functional devices. Several structures are discussed such as layered arrays of gold nanoparticles, core-shell structures and hierarchical structures. The optical properties of these structures are also presented and compared with simulations. Some of the structures are of interest for plasmonic cloaking whereas other might find applications as substrates for sensing by surface-enhanced Raman spectroscopy.

T. Bürgi and A. Cunningham, *Proc. SPIE* 8423, 842318 (2012).

Induction of Thermotropic Bicontinuous Cubic Phases in Liquid-Crystalline Ammonium and Phosphonium Salts. Two series of wedge-shaped onium salts, having 3,4,5-tris(alkyloxy)benzyl moieties, exhibit thermotropic bicontinuous "gyroid" cubic (Cub_{bi}) and hexagonal columnar liquid-crystalline (LC) phases by nanosegregation between ionophilic and ionophobic parts. The alkyl chain lengths on the cationic moieties, anion species, and alkyl chain lengths on the benzyl moieties have crucial effects on their thermotropic phase behavior. Synchrotron small-angle diffraction intensities from the Cub_{bi} LC materials provide electron density maps in the bulk state. A novel differential mapping technique has been applied successfully mapping out the location of the ionic species in the unit cell. The Cub_{bi} LC materials exhibit efficient ion-transporting behavior as a result of their 3D interconnected ion nanochannel networks. The Cub_{bi} LC material formed by triethyl-[3,4,5-tris(decyloxy)benzyl]phosphonium tetrafluoroborate shows ionic conductivities higher than the analogous Cub_{bi} material based on ammonium salts. The present study indicates great potential of Cub_{bi} LC nanostructures consisting of ionic molecules for development of transportation nanochannel materials.

T. Ichikawa, M Yoshio, A. Hamasaki, S. Taguchi, F. Liu, X. Zeng, G. Ungar, H. Ohno, T. Kato, *J. Am. Chem. Soc.,* 134, 2634-2643 (2012).

Two- and Three-Dimensional Liquid-Crystal Phases from Axial Bundles of Rodlike Polyphiles: Segmented Cylinders, Crossed Columns, and Ribbons between Sheets. Rodlike mesogens (see scheme) with swallow-tail side chains arrange axially in ribbonlike bundles. At high temperatures the ribbons rotate, resulting in a novel 3D hexagonal liquid-crystal phase. At lower temperature, rotation locks in giving a structure of crossed aromatic and fluorinated columns. On further cooling the ribbons fuse into aromatic sheets with fluorinated columns intercalated.

F. Liu, M. Prehm, X.B. Zeng, G. Ungar, C. Tschierske, *Angew. Chem. Int. Ed.*, 50, 10599-10602 (2011).

Simple Cubic Superlattice of Gold Nanoparticles through Rational Design of their Dendrimeric Corona. The first simple-cubic liquid crystal was obtained by coating monodisperse Au nanoparticles (NPs) with a thick corona of amino-substituted organic dendrons. This unusual structure was determined by grazing-incidence diffraction and electron density reconstruction and explained by analyzing the radial density profile of the corona. Another novel structure is proposed for the phase preceding the cubic one: a hexagonal superlattice composed of alternating dense and sparse strings of Au NPs.

K. Kanie, M. Matsubara, X.B. Zeng, F. Liu, G. Ungar, H. Nakamura, A. Muramatsu, *J. Am. Chem. Soc.*, 134 (2), 808-811 (2012).

Electro-Functional Octupolar p-Conjugated Columnar Liquid Crystals. A series of propeller-shaped π-conjugated molecules based on 2,4,6-tris(thiophene-2-yl)-1,3,5-triazines has been designed and synthesized to obtain ambipolar charge-transporting liquid-crystalline materials. The 3-fold electron-donating aromatic units are attached to the electron-accepting triazine core, which forms electro-functional octupolar π-conjugated structures. These octupolar molecules self-organize into one-dimensional columnar nanostructures and exhibit ambipolar carrier transport behavior, which has been revealed by time-of-flight measurements. In this approach, electron-donor and acceptor electro-active segments are assembled individually in each column to give one-dimensional nanostructured materials with precisely tuned electronic properties. Their desirable electronic structures responsible for both hole and electron conductions have also been examined by cyclic voltammetry and theoretical calculations. The present results provide a new guideline and versatile approach to the design of ambipolar conductive nanostructured liquid-crystalline materials.

T. Yasuda, T. Shimizu, F. Liu, G. Ungar, T. Kato, *J. Am. Chem. Soc.,* 133, 13437–13444 (2011).

Self-Repairing Complex Helical Columns Generated via Kinetically Controlled Self-Assembly of Dendronized Perylene Bisimides. The dendronized perylene 3,4:9,10-tetracarboxylic acid bisimide (PBI), (3,4,5)12G1-3-PBI, was recently reported to selfassemble in complex helical columns containing tetramers of PBI as basic repeat unit. These tetramers contain a pair of two molecules arranged side-by-side and another pair in the next stratum of the column turned upside-down and rotated around the column axis. Intra- and intertetramer rotation angles and stacking distances are different. At high temperature, (3,4,5)12G1-3-PBI self-assembles into a 2D hexagonal columnar phase while at low temperature it forms a 3D orthorhombic columnar array. Here, we report the synthesis and structural analysis, by a combination of DSC, X-ray and electron diffraction, and solid-state NMR, on the supramolecular structures of a library of (3,4,5)nG1-3-PBI with n = 14–4. We highlight the fact that at low temperatures for n = 9, 8 a thermodynamically stable monoclinic structure forms, that is a self-repairing helical columnar array with both the intra- and intertetramer distances of 3.5 Å. This stable low-temperature structure promises with regular and close pi-pi contacts promises to provide efficient and reliable charge carrier mobility. This discovery is important for the field of self-assembly and for the molecular design of supramolecular materials for electronics and solar cells.

V. Percec, S.D. Hudson, M. Peterca, P. Leowanawat, E. Aqad, R. Graf, H.W. Spiess, X.B. Zeng, G. Ungar, P.A. Heiney, *J. Am. Chem. Soc.*, 133, 18479-18494 (2011).

Liquid Quasicrystals. In the first part, this brief review discusses the discovery of the first example of supramolecular dendritic liquid quasicrystal, which represents also the first example of soft quasicrystal. In the second part, we show that soft quasicrystals generated from supramolecular spheres are scattered through libraries of self-assembling dendrons, dendrimers, and dendronized polymers. The supramolecular spheres forming soft quasicrystals are generated via at least two different mechanisms, and are chiral. Generation of quasicrystals from other organic building blocks is also discussed. Finally, potential applications in electronics, sensors, and as ionic liquid-based nanoreactors are also mentioned.

G. Ungar, V. Percec, X.B. Zeng, P. Leowanawat, invited review on the occasion of the Nobel Prize award to D. Shechtman, *Israel J. Chem*., 51, 1206-1215 (2011).

1.3. WP3 - Characterization of optical properties and verification of structures

Summary of work progress and main achievements for project NANOGOLD

- The plasmon coupling within assemblies of larger gold nanoparticles was analyzed for different structures by comparing UV-vis extinction spectra and simulations of analogous structures. Optical characteristics were determined of silver nanoparticle thin films as part of the development of plasmonic ink.

- Core-shell nanostructures were fabricated by self-assembly and their structure determined by electron microscopy, grazing-incidence XRD and X-ray reflectivity. Based on that a geometrical model was established that served as the basis for simulations of the optical properties. The nanostructure exhibits a strong and isotropic magnetic response in the visible spectrum. The optical properties of such complex plasmonic particles were analyzed in terms of their viability for creating negative magnetis permeability, a precondition for negative refractive index. The magnetic response was also directly confirmed by Fourier microscopy of single core-shell particle and by other optical experiments.

- Nanoparticle double layers separated by polymer multilayers were studied experimentally and theoretically. Strong shifts of plasmonic resonance were observed for close layers and explained theoretically in terms of band splitting into bonding and nonbonding. It was shown that the spectral features can be explained to a large extent merely by coherent interaction between neighbouring NPs. Asymmetric bilayers, e.g. gold and silver layers were shown to potentially form media with strongly enhanced magnetic resonance. A combination of NPs and optical cavity was shown theoretically and experimentally to exhibit strong photon-plasmon interaction, leading to prototype sensing and light-emitting devices.

- A tractable molecular field theory was developed for predicting the phase diagram of binary systems of spheres and rods/discs. The theory predicts isotropic, nematic, smectic and columnar phases. The study reveals a series of principles to apply when designing LC dispersions of NPs. Atomic scale models of gold NPs covered with mesogenic ligands were subjected to dynamics simulation, which helped understand the experimental findings and design new ordered superlattices.

- A series of mesogen-covered gold NPs, with different nematogenic and dendritic ligands and alkylthiol coligand were studied by XRD and TEM and their numerous new structures determined. Conditions for achieving anisotropic superlattices were established and ways to control interparticle spacing in NP strings as a way to tune the plasmonic resonance. First helical 3-d ordered NP arrays were achieved using cholesteric mesogens for interaction with circularly polarized light.

A bottom-up apporach to fabricate optical metamaterials by self-assembled metallic nanoparticles. We introduce a novel bottom-up approach to fabricate by self assembly a metamaterial from metallic nanoparticles in a two-step process. In the first step, a metamaterial made of densely packed silver nanoparticles is required. The material dispersion with increasing nanoparticle densities, from dispersed to randomly packed nanoparticles, was measured by spectroscopic ellipsometry, demonstrating high

permittivity values in the visible. In the second step, this material was used to prepare spherical clusters by a method based on oil-in-water emulsion. The optical properties of these clusters were equally investigated by spectroscopic means. Comparisons with rigorous numerical simulations clearly indicate that, depending on the cluster size, their spectral response can be unambiguously associated with the excitation of a magnetic dipole resonance. As a consequence, such spherical clusters are promising building blocks for future metamaterials possessing a magnetic response in the visible range.

J. Dintinger, S. Mühlig, C. Rockstuhl, T. Scharf, Opt. Mat. Exp., 2, 269-278, (2012).

*Self-Assembled Plasmonic Core-Shell Clusters with an Isotropic Magnetic Dipole Response in the Visible Range***.** We theoretically analyze, fabricate, and characterize a three-dimensional plasmonic nanostructure that exhibits a strong and isotropic magnetic response in the visible spectral domain. Using two different bottom-up approaches that rely on self-organization and colloidal nanochemistry, we fabricate clusters consisting of dielectric core spheres, which are smaller than the wavelength of the incident radiation and are decorated by a large number of metallic nanospheres. Hence, despite having a complicated inner geometry, such a core–shell particle is sufficiently small to be perceived as an individual object in the far field. The optical properties of such complex plasmonic core–shell particles are discussed for two different core diameters.

S. Mühlig, A. Cunningham, S. Scheeler, C. Pacholski, T. Burgi, C. Rockstuhl, and F. Lederer, *ACS Nano*, 5, 6586 (2011).

Coupling of plasmon resonances in tunable layered arrays of gold nanoparticles. Using bottom-up and self-assembly processes, large scale layered arrays of strongly coupled gold nanoparticles with controllable dimensions were fabricated. By carefully adjusting the distance between adjacent gold nanoparticle arrays, it is possible to control the coupling of the localized surface plasmon polariton resonance as sustained by individual gold nanoparticles. A greater interaction is observed at smaller separations, leading to a well pronounced shift in the spectral position of resonances that can be adjusted with high precision. Simulations showed good agreement with experimental observations in an in-depth investigation of such structures, suggesting minimal separations of only one nanometer are achieved.

A. Cunningham, S. Mühlig, C. Rockstuhl, and T. Bürgi, *Journal of Physical Chemistry C*, Vol. 115, 8955 (2011).

*Effects of anisotropic disorder in an optical metamaterial***.** We consider the effect of disorder in one transverse dimension, termed anisotropic disorder, on the optical properties of a metamaterial consisting of cut-wire-pair meta-atoms. The work comprises experimental and numerical studies. The appropriate samples were fabricated and their optical properties quantified in the far-field. For comparison large-scale rigorous numerical simulations were performed. We observe excellent agreement between experiment and theory. Based on our results we reveal how the electric dipole interactions between adjacent meta-atoms affect the overall spectral response of the metamaterial. Our main observation is a polarization-sensitive degradation of the symmetric resonance for anisotropic disorder.

C. Helgert, C. Rockstuhl, C. Etrich, E.-B. Kley, A. Tünnermann, F. Lederer, and T. Pertsch, *Applied Physics A*, 103, 591, (2011)

*Optical properties of a fabricated self-assembled bottom-up bulk metamaterial***.** We investigate the optical properties of a true three-dimensional metamaterial that was fabricated using a self-assembly bottom-up technology. The metamaterial consists of closely packed spherical clusters being formed by a large number of non-touching gold nanoparticles. After presenting experimental results, we apply a generalized Mie theory to analyze its spectral response revealing that it is dominated by a magnetic dipole contribution. By using an effective medium theory we show that the fabricated metamaterial exhibits a dispersive effective permeability, i.e. artificial magnetism. Although this metamaterial is not yet left-handed it might serve as a starting point for achieving bulk metamaterials by using bottom-up approaches.

S. Mühlig, C. Rockstuhl, V. Yannopapas, T. Bürgi, N. Shalkevich, and F. Lederer, *Optics Express*, Vol. 19, 9607 (2011).

In situ polarized micro-Raman investigation of periodic structures realized in liquid-crystalline composite materials. In situ polarized micro-Raman Spectroscopy has been utilized to determine the liquid crystal configuration inside a periodic liquid crystalline composite structure made of polymer slices alternated to films of liquid crystal. Liquid crystal, Norland Optical Adhesive (NOA-61) monomer and its polymerized form have been investigated separately. The main Raman features, used as markers for the molecular orientation estimation, have been identified. In situ polarized Raman spectra indicate that the orientation of the liquid crystal director inside the structure is perpendicular to its polymeric slices. Results show the usefulness of in situ polarized micro-Raman spectroscopy to investigate liquid crystalline composite structures.

M. Castriota, A. Fasanella, E. Cazzanelli, L. De Sio, R. Caputo, and C. Umeton, *Optics Express*, Vol. 19, 10494 (2011).

1.4. WP4 - Design and analysis of optical materials, organization, and functionalities

The nanoamterials the Nanogold project focused on are fundamentally different to established nanoamterials which are usually fabricated with top-down approaches. Top-down approaches lead to highly deterministic, strictly periodically arranged meta-atoms which possess an identical shape that can usually be described by a few geometrical parameters only. In opposite, our nanomaterials are made from amorphous arrangements of meta-atoms with a highly complicated geometry that are made from a larger number of metallic nanoparticles. For these meta-atoms only a nominal geometry can be identified but not the exact shape it possesses. The combination of all these aspects requires novel means to disclose the optical properties and to assign eventually effective ones. Solutions to these challenges were found in the project. In particular, the following achievements are reported:

- *Scattering properties of individual meta-atoms:* A language had to be developed to discuss the optical action of meta-atoms and to consider them in further simulations that consider the entire material. The first part was successfully accomplished by developing a mathematical language to express the scattering response of arbitrary meta-atoms in terms of multipoles. This allows to analyze rather instantly which kind of character a meta-atom possesses. Moreover, the entire T-matrix of meta-atoms has been calculated. It permits to predict reliably its optical response to an arbitrary illumination and allows considering it in further simulations that are used to disclose bulk properties of an entire material.

- *Assigning effective properties:* Using the information from the achievement above, various novel techniques were developed and the applicability of established tools has been verified to assign effective properties to the amorphous materials of interest. This comprises the application of Clausius-Mossotti effective medium theory whose predictions were compared to larger scale simulations of amorphous structures, the considerations of the meta-atoms in a scattering code that can calculate reflection and transmission from stacks and, moreover, the calculation of the dispersion relation of Bloch modes. From this analysis many conclusions can be drawn and genuine predictions were made such as, e.g., the occurrence of Dirac points in the dispersion relation of the metamaterials. Moreover, not just classical material parameters were discussed but more advanced as well. Examples are the effective chirality of a metamaterial, the emergence of gapless surface modes, and the emergence of Faraday rotation.

- *New functionalities beyond material properties*: Besides the assignment of effective properties to the materials made from our meta-atoms, we have investigated by different approaches new functionalities that can be directly implemented with the meta-atoms at our disposal. These applications rely on the exploitation of, e.g., the peculiar scattering response of the meta-atoms or their ability to localize electromagnetic energy to an extraordinary degree in their near-field. The application we have pioneered are, e.g., cloaking device which allow to conceal an object from an external observer. Our approach bases on the cancelation of the scattering response and it can be used to cloak electrically small object but also more extended objects. Other more primary applications are discrete diffraction in novel waveguides and substrates for surface enhanced Raman scattering. They are all documented in more detail on the following pages.

Ordered arrays of metal nanostrings as broadband super absorbers. We study the absorption spectrum of ordered arrays of strings of gold nanoparticles within a nematic liquid crystal by a rigorous electrodynamic approach. We find, in particular, that, as the length of the strings increases, light absorbance can be very high over the entire visible regime. The ordinary modes of the nematic liquid crystal allow the nanoparticle strings to absorb light much more efficiently than the extraordinary modes. Overall, absorption does not depend on the lattice type of the string array due to the subwavelength functionality of the system. Such a structure operates as a gray body exhibiting an absorption efficiency of 79% within the entire visible regime, averaging over all angles of incidence and polarization modes.

V. Yannopapas and I. E. Psarobas, *J. Phys. Chem. C*, 116, 15599 (2012).

Effective electric and magnetic properties of metasurfaces in transition from crystalline to amorphous state. In this paper we theoretically study electromagnetic reflection, transmission, and scattering properties of periodic and random arrays of particles which exhibit both electric-mode and magnetic-mode resonances. We compare the properties of regular and random grids and explain recently observed dramatic differences in resonance broadening in the electric and magnetic modes of random arrays. We show that randomness in the particle positioning influences equally on the scattering loss from both electric and magnetic dipoles, however, the observed resonance broadening can be very different depending on the absorption level in different modes as well as on the average electrical distance between the particles. The theory is illustrated by an

example of a planar metasurface composed of cut-wire pairs. We show that in this particular case at the magnetic resonance the array response is almost not affected by positioning randomness due to lower frequency and higher absorption losses in that mode. The developed model allows predictions of behavior of random grids based on the knowledge of polarizabilities of single inclusions.

M. Albooyeh, D. Morits, and S. Tretyakov, *Phys. Rev. B*, vol. 85, p. 205110 (2012).

Plasmon-induced enhancement of nonlinear optical rectification in organic materials. We show that nonlinear optical rectification (NOR) can be greatly enhanced in the proximity of plasmonic nanostructures. The NOR enhancement in the visible frequency range near Cu-coated SiO2 nanospheres is calculated by a rigorous first-principle electromagnetic Green's tensor technique. Exemplary compounds with absorption in the visible optical spectrum based on and metalloporphyrin molecules are discussed, exhibiting enhancement factors typically larger than ten. Their spectral properties in relation to NOR are obtained by first-principle electronic structure calculations.

I. Thanopulos, E. Paspalakis, and V. Yannopapas, *Phys. Rev. B*, 85, 035111 (2012).

Lasing action in multilayers of alternating monolayers of metallic nanoparticles and dielectric slabs with gain. By employing a rigorous multiple-scattering electrodynamic approach we study the loss compensation and lasing action in photonic crystals formed as alternating layers of active dielectric slabs and two-dimensional planes of plasmonic (metallic) spheres. The strong dispersion of the plasmonic bands and the efficient trapping of light among the dielectric slabs (the cavity effect) triggers lasing action for thin slabs of the photonic crystal and for a moderate amount of gain, with quality factors of the order of 103. Below and above the lasing threshold, gain compensates losses, promising significant improvement of the imaging properties of plasmonic photonic crystals.

V. Yannopapas and I. E. Psarobas, *J. Opt.*, 14, 035101 (2012).

Scattering cancellation of the magnetic dipole field from macroscopic spheres. Based on the scattering cancellation technique we suggest a cloak that allows to conceal macroscopic objects, i.e. objects with an optical size comparable to wavelengths in the visible and whose scattering response is dominated by a magnetic dipole contribution. The key idea in our approach is to use a shell of polaritonic spheres around the object to be cloaked. These spheres exhibit an artificial magnetism. In a systematic investigation, where we progressively increase the complexity of the considered structure, we devise the requirements imposed on the shell and outline how it can be implemented with natural available materials.

M. Farhat, S. Mühlig, C. Rockstuhl, and F. Lederer, *Optics Express*, 20 13896- 13906 (2012).

Photonic nanojets as three-dimensional optical atom traps: A theoretical study. We show that an efficient three-dimensional optical atom trap can be achieved by light scattered off a dielectric microsphere. Namely, under suitable conditions, a plane wave incident on a polymer sphere produces a focal point in the forward scattering direction known as photonic nanojet. The photonic nanojet is formed at a distance of a few micrometers away from the surface of the sphere wherein the Casimir–Polder interaction felt by an atom is negligible compared to the optical and gravitational potentials. When many polymer spheres are brought together so as to form a linear chain, a one-dimensional periodic optical lattice filled with cold atoms is possible since

interference between the incident and scattered beams is minimal when the spheres are not too close.

V. Yannopapas, *Opt. Commun.*, 285, 2952 (2012).

Multipode Analysis of Meta-Atoms. We determine the rigorously calculated scattered field of meta-atoms and decompose it into spherical harmonics with complex amplitudes. Transforming these spherical harmonics into a Cartesian base reveals all multipole moments in this coordinate system, i.e. all electric and magnetic dipole, quadrupole and any higher order moments can be completely determined. We show that these multipole moments provide a deeper understanding on how light interacts with the considered meta-atoms. After sketching the analytical framework, we investigate exemplarily two well-established meta-atoms and show the applicability of our approach.

S. Mühlig, C. Menzel, C. Rockstuhl and F. Lederer, *Metamaterials*, 5, 64-73 (2011).

Enhancement of ultraviolet photoinduced energy transfer near plasmonic nanostuctures. We show that photoinduced intermolecular energy transfer can be greatly enhanced in the UV frequency range in proximity to plasmonic metamaterials. The rate of the resonance energy transfer for a molecular donor−acceptor system with absorption and emission transition lines in the vacuum UV near metal-coated dielectric nanospheres is calculated by a rigorous first-principle electromagnetic Green's tensor technique. Exemplary donor−acceptor systems based on fullerenes and organic compounds are discussed. The electronic transition spectra of the donor−acceptor molecules are obtained by ab initio calculations.

I. thanopulos, E. Paspalakis, and V. Yannopapas, *J. Phys. Chem. C*, 115, 4370 (2011).

Scattering properties of metaatoms. Metamaterials consist of a periodic or aperiodic arrangement of so-called meta-atoms. Usually their optical properties are derived from the collective response of this ensemble. However, it is highly desirable to deduce them from the scattering properties of individual meta-atoms because frequently the periodic arrangement has a spurious effect on the desired functionality. Moreover, understanding the scattering properties of individual meta-atoms permits introducing guidelines for their design and predicting effective properties of amorphous metamaterials. To achieve this we introduce a genuine approach to quantify the properties of individual meta-atoms. To this end we evaluate spectrally resolved the composition of the rigorously calculated scattered field in terms of contributions of electromagnetic multipoles, such as electric and magnetic dipoles, quadrupoles and, in principle, arbitrary higher order moments. Beyond its direct application to metamaterial's design and characterization, the approach will be significant in the entire field of nanooptics as, for example, for optical nanoantennas.

C. Rockstuhl, C. Menzel, S. Mühlig, J. Petschulat, C. Helgert, C. Etrich, A. Chipouline, T. Pertsch, and F. Lederer, *Physical Review B*, 83, 245119 (2011).

Understanding the functionality of an array of invisibility cloaks. This paper describes the operation and the interaction of cloaking devices when they are periodically arranged. The main focus is on analyzing the dispersion relation of structures, which should mimic that of the vacuum in the ideal scenario. We distinguish between two cloaking mechanisms: cloaks designed within the framework of transformation optics and cloaks designed on the basis of the scattering cancellation technique. The

difference between the two approaches is that the first operates independently of the frequency by assuming nondispersive materials, whereas the latter is designed to operate for a single frequency. Our numerical simulations demonstrate that arrays made of such invisible dielectric obstacles act like a homogeneous medium with permittivity and permeability equal to those of the surrounding medium, except for a countable set of eigenfrequencies associated with Mie resonances for the former type of (transformation-based) cloak. For the latter type of (plasmonic) cloak, the marginal scattering response indicates the effectiveness of cloaking arrays of individual particles. Our spectral (Floquet-Bloch) approach to cloaking might be useful to implement realistic applications such as biomedical sensing, noninvasive probing, sensing networks, or multiobjective camouflaging.

M. Farhat, P. Yen Chen, S. Guenneau, S. Enoch, R, McPhedran, C. Rockstuhl, and F. Lederer, *Physical Review B*, Vol. 84, 235105 (2011).

Cloaking dielectric spherical objects by a shell of metallic nanoparticles. We show that dielectric spheres can be cloaked by a shell of amorphously arranged metallic nanoparticles. The shell represents an artificial medium with tunable effective properties that can be adjusted such that the scattered signals of shell and sphere almost cancel each other. We provide an analytical model for the cloak design and prove numerically that the cloak operates as desired. We show that more than 70% of the scattered signal of the sphere can be suppressed at the design wavelength. Advantages and disadvantages of such a cloak when compared to other implementations are disclosed.

S. Mühlig, M. Farhat, C. Rockstuhl, and F. Lederer, *Phys. Rev. B*, Vol. 83, 195116 (2011).

Gapless surface states in a lattice of coupled cavities: A photonic analog of topological crystalline insulators. We show that a tetragonal lattice of weakly interacting cavities with uniaxial electromagnetic response is the photonic counterpart of topological crystalline insulators, a new topological phase of atomic band insulators. Namely, the frequency band structure stemming from the interaction of resonant modes of the individual cavities exhibits an omnidirectional band gap within which gapless surface states emerge for finite slabs of the lattice. Due to the equivalence of a topological crystalline insulator with its photonic-crystal analog, the frequency band structure of the latter can be characterized by a Z2 topological invariant. Such a topological photonic crystal can be realized in the microwave regime as a three-dimensional lattice of dielectric particles embedded within a continuous network of thin metallic wires.

V. Yannopapas, *Phys. Rev. B*, 84, 195126 (2011).

Photonic analog of a spin-polarized system with Rashba spin-orbit coupling. We show that a gyrotropic (chiral) medium supporting a longitudinal-wave excitation exhibits a Dirac point in the corresponding photon dispersion lines. By breaking the time-reversal symmetry in such a medium, the dispersion relation resembles the energy dispersion of a spin-polarized two-dimensional electron gas with Rashba spin-orbit coupling. The resulting split bands of the dispersion relation correspond to nonzero Chern numbers implying the existence of nontrivial topological states of the electromagnetic field.

V. Yannopapas, *Phys. Rev. B*, 83, 113101 (2011).

Dirac point in the photon dispersion relation of a negative/zero/positive-index plasmonic metamaterial. We report on the emergence of a Dirac point in the dispersion relation of a plasmonic metamaterial. It is realized as a three-dimensional crystal (cubic or orthorhombic) whose lattice sites are decorated by aggregates of gold nanoparticles embedded in a high-index dielectric material. The Dirac-type dispersion lines of the photon modes are not a result of diffraction as in photonic crystals but due to subwavelength features and emerge from the gapless transition from a negative to a positive index band. The Dirac point is manifested as a dip in the spectrum of light transmittance through a finite slab of the metamaterial; however, transmittance does not decrease diffusively but exponentially due to the inherent losses of gold in the given spectral regime.

V. Yannopapas and A.G. Vanakaras, *Phys. Rev. B*, 84, 045128 (2011).

A hybrid layer-multiple-scattering/Fourier modal method for photonic structures based on lithographic and/or self-assembly techniques. We present a new scattering method which allows for the calculation of the optical properties of lithography- and self-assembly-based photonic nanostructures. The lithographic components are modelled by the Fourier modal method while the self-assembly-based ones by the layer-multiple-scattering method. The key property which allows the merging of both theoretical methods into a common programming code are the scattering (transmission/reflection) matrices for a finite photonic slab. In order to demonstrate the potential of this new, hybrid method we study light absorption by a two-dimensional lattice of metallic rods with square cross-section sitting atop a homogeneous substrate and a two-dimensional lattice of dielectric spheres.

V. Yannopapas, *Journal of Modern Optics*, Vol. 58, 400 (2011).

Three-dimensional metamaterial nanotips. We investigate the optical properties of a three-dimensional metamaterial nanotip that has a pyramidal shape. The nanotip itself is made of a large number of densely packed metallic nanospheres. In analogy to the emergence of a continuous energy band in a crystal, the strong coupling among neighboring nanospheres forces them to act collectively and allows the observation of a broad plasmonic band. The largely increased degrees of freedom within the metamaterial nanotip allow sustaining a great variety of different localized eigenmodes. In this contribution, we systematically reveal their peculiar polarization state and show that they allow for light localization in various well-defined spatial domains.

S. Mühlig, C. Rockstuhl, J. Pniewski, C. R. Simovski, S. A. Tretyakov, and F. Lederer, *Physical Review B*, Vol 81, 075317 (2010).

*Validity of effective material parameters for optical fishnet metamaterials***.** Although optical metamaterials that show artificial magnetism are mesoscopic systems, they are frequently described in terms of effective material parameters. But due to intrinsic nonlocal (or spatially dispersive) effects it may be anticipated that this approach is usually only a crude approximation and is physically meaningless. In order to study the limitations regarding the assignment of effective material parameters, we present a technique to retrieve the frequency-dependent elements of the effective permittivity and permeability tensors for arbitrary angles of incidence and apply the method exemplarily to the fishnet metamaterial. It turns out that for the fishnet metamaterial, genuine effective material parameters can only be introduced if quite stringent constraints are imposed on the wavelength/unit cell size ratio. Unfortunately they are only met far away

from the resonances that induce a magnetic response required for many envisioned applications of such a fishnet metamaterial. Our work clearly indicates that the mesoscopic nature and the related spatial dispersion of contemporary optical metamaterials that show artificial magnetism prohibits the meaningful introduction of conventional effective material parameters.

C. Menzel, T. Paul, C. Rockstuhl, T. Pertsch, S. Tretyakov, and F. Lederer, *Physical Review B*, Vol 81, 035320 (2010).

Backward propagating slow light in Mie resonance based metamaterials. We show theoretically that electromagnetic radiation within Mie-based metamaterials can have a negative refractive index and, at the same time, propagate with a group velocity that is of the order of 105 slower than the vacuum one. In the infrared regime, such behaviour is achieved for metamaterials made from binary superlattices of polaritonic and plasmonic microspheres, whilst in the optical regime it is demonstrated for metal-coated semiconductor nanospheres. The results presented are based on rigorous calculations of the frequency band structure of the above metamaterials obtained by the layer multiple-scattering method.

V. Yannopapas and E. Paspalakis, *J. Opt.*, Vol. 12, 104017 (2010).

*Understanding the electric and magnetic response of isolated metaatoms by means of a multipolar field decomposition***.** We introduce a technique to decompose the scattered near field of two-dimensional arbitrary metaatoms into its multipole contributions. To this end we expand the scattered field upon plane wave illumination into cylindrical harmonics as known from Mie's theory. By relating these cylindrical harmonics to the field radiated by Cartesian multipoles, the contribution of the lowest order electric and magnetic multipoles can be identified. Revealing these multipoles is essential for the design of metamaterials because they largely determine the character of light propagation. In particular, having this information at hand it is straightforward to distinguish between effects that result either from the arrangement of the metaatoms or from their particular design.

J. Petschulat, J. Yang, C. Menzel, C. Rockstuhl, A. Chipouline, P. Lalanne, A. Tünnermann, F. Lederer, and T. Pertsch, *Optics Express*, Vol 18, 14454 (2010).

1.5. WP5 - Implementation and testing of applications based on metamaterials with macromolecules

Work package 5 was entirely dedicated to technology and applications. Three concrete tasks were defined to structure the work and define research schemes of highest potential: creation of nanostructured composite metamaterials, strategies of cloaking objects for different geometries and explore the wave propagation and realization of a metamaterial-dielectric multilayer device. The three tasks were attacked with different technological strategies: combine liquid crystal technology and plasmonic nanoparticle resonances in polymer dispersed liquid crystals (PDLC), design and realize dense materials with core shell concepts based on dielectric and metallic nanoparticles and build up bulk assemblies by layer-by-layer deposition of optical material and nanoparticle cluster matter.

A major part of achievements could be done by using a particular technology called POLICRYPS. POLICRYPS (an acronym of polymer liquid crystal polymer slices) is a nano/microcomposite structure made of slices of almost pure polymer alternated with

films of well aligned liquid crystal. The liquid crystalline material can be in different phases such as nematic, cholesteric or smectic. Even templating by washing out parts of the structures is possible and the effort here was concentrated on regular structures that could be produced with spatial periods varying from 200 nm to 20 µm. The combination with high refractive index resonant particles allowed to access new optical phenomena based on wave guiding, coupled modes and plasmon resonances.

Based on a particular electrochemical deposition technique meta-atoms could be produced and densified layers of such meta-atoms could be demonstrated. Because a metaatom gets its electromagnetic properties from its structural properties and its composition amorphous material layers could be design to suppress optical scattering effects due to its very nature in a certain wavelength range. Here the combination of Mie scattering and plasmon resonance gives the metaatom its functional properties. Suppression of scattering is one of the major topics of research because of its impact on lossless information transmission and optical circuit design. Dense films of amorphous metaatom material were produced and evaluated with success.

In a more classical approach we studied Bragg multilayer reflection in combination with cluster matter which combines plasmon resonances of nanoparticles with interference in multilayers. A particular challenge is the application of high density nanoparticle cluster matter and the conservation of the resonance properties during processing. Different methods are studied and applied to realize films that show strong reflectivity effects based on the combined optical effects. A large parameter spaces to tune the optical properties was made available and detailed characterisation of the multilayer devices is documented.

The variety of approaches used in WP5 led to synergies between different techniques and made the transfer of technology possible between them. Due to the combination of different materials favourable situation for device fabrication and exploitation of different materials could be created. Materials realized in WP1 and WP2 could be transferred to technology tests. Functional devices realized here were characterised and qualified in WP3 and results were discussed and analyzed by WP4 to give feedback on critical geometrical parameters and material constants.

Longitudinal-differential interferometry: Direct imaging of axial superluminal phase propagation. We introduce and demonstrate a new interferometric method called longitudinal-differential (LD) interferometry, which measures the spatially resolved phase difference of the scattered field by an object relative to the illumination. This method is combined with a high-resolution interference microscope that allows recording three-dimensional field distributions in amplitude and phase. The method is applied to study the axial phase behavior of Arago spots, an effect observable in low-Fresnel-number systems behind objects with a size comparable to the wavelength. We directly observe the initial phase delay in the Arago spot and prove that the local phase velocity exceeds the speed of light in air. Such LD phase studies are applicable not only to the Arago spot but also to other kinds of light interactions with wavelength-scale objects, e.g., photonic nanojets.

M.-S. Kim, T. Scharf, C. Etrich, C. Rockstul, and H. P. Herzig, *Opt. Lett.*, 37, 305-307 (2012).

Realization and Characterization of POLICRYPS-like Structures Including Metallic Subentities. A first characterization of newly realized micro periodic structures including metallic nanoparticles is reported. The original mixture, generally utilized for the realization of polymer-liquid-crystal-polymer-slices gratings (POLICRYPS), has been enriched with a small amount of silver nanoparticles. The obtained structure shows a spectral response that strongly depends on the polarization of the probing light. These first structures are oriented to the fabrication of devices with metamaterial properties.

R. Caputo, L. De Sio, J. Dintinger, H. Sellame, T. Scharf, and C. P. Umeton, *Mol. Cryst. Liq. Cryst.*, 553, 111-117 (2012).

Plasmon resonance tunability of Gold nanoparticles embedded in a confined Cholesteric Liquid Crystal host. Gold nanoparticles have been dissolved in a cholesteric liquid crystal and then infiltrated in a micro-periodic polymeric structure. This has been realized by combining a holographic step and a microfluidic etching process. The spectral behavior of the nano-composite soft-structure has been investigated in the UV-Vis range for two different polarization directions of an impinging probe light and in presence of external perturbations (electric field, temperature variation). Obtained results show a highly tunable plasmonic response of the material.

R. Caputo, L. De Sio, U. Cataldi, and C. Umeton, *Mol. Cryst. Liq. Cryst*., 559, 194-201 (2012).

Molecular Orientation of E7 Liquid Crystal in POLICRYPS Holographic Gratings: A Micro-Raman Spectroscopic Analysis. Micro-Raman Spectroscopy was used to determine the orientation of the E7 nematic liquid crystal molecules inside the POLICRYPS (POlymer LIquid CRYstal Polymer Slices) holographic gratings. The POLICRYPS grating was analyzed after defining the Raman features of each single component of the system: i.e the random aligned nematic liquid crystal E7 and Norland Optical Adhesive (NOA-61). Among the Raman bands of the liquid crystal molecules, a specific one was selected, which exhibits strong anisotropy of the Raman tensor. The modulation of its intensity, depending on the sample orientation with respect to the laser polarization, provided the experimental evidence about the orientation of the E7 molecules, which occurred to be perpendicular to the polymeric slices.

A. Fasanella, M. Castriota, E. Cazzanelli, L. De Sio, R. Caputo, and C. Umeton, *Mol. Cryst. Liq. Cryst.*, 558, 46-53 (2012).

*Fabrication and Characterization of Stretchable PDMS Structures Doped with Au Nanoparticles***.** Fabrication of samples showing plasmonic properties is a fundamental step towards the realization of devices that can exhibit peculiar electromagnetic properties. In this work we illustrate some fabrication techniques that can reveal useful for the realization of this kind of samples. For what concerns materials, we used polydimethylsiloxane (PDMS) combined with Au nanoparticles (NPs). A first experimental characterization of the obtained structures has been reported.

U. Cataldi, P. Cerminara, L. De Sio, R. Caputo and C. Umeton, *Mol. Cryst. Liq. Cryst.*, 558, 22-27 (2012).

Optical properties of mesogen-coated gold nanoparticles. In this work, the physical and optical properties of gold nanoparticles functionalized with laterally grafted nematic ligands were studied. In particular, the influence of the nanoparticle size on the mesomorphic behavior and optical properties of the composite was investigated. To obtain an in-plane alignment of the mesogens, thin oriented films were prepared by shearing and characterized by polarized absorption spectroscopy. While the sub-2nm nanoparticle thin film only showed birefringence due to a strong damping of the plasmon resonance, larger NPs exhibit a strong dichroism with a shift of the NP plasmon resonance by about 50 nm. These results demonstrate the possibility to obtain a bulk NP metamaterial with tunable plasmonic properties by chemical engineering of the NP ligands.

J. Dintinger, B.J. Tang, X. Zeng, T. Kienzler, G. H. Mehl, G. Ungar, C. Rockstuh,l and T. Scharf, *Proc. SPIE 8271*, 827106 (2012).

Plasmonic nanoparticles for a bottom-up approach to fabricate optical metamaterials. We investigate experimentally metallic nanoparticle composites fabricated by bottom-up techniques as potential candidates for optical metamaterials. Depending on the plasmonic resonances sustained by individual NPs and their nanoscale organization into larger meta-atoms, various properties might emerge. Here, the focus of our contribution is on the fabrication and optical characterization of silver NP clusters with a spherical shape. We start with the characterisation of the "bulk" dielectric constants of silver NP inks by spectroscopic ellipsometry for different nanoparticle densities (i.e from strongly diluted dispersions to solid randomly packed films). The inks are then used to prepare spherical nanoparticle clusters by an oil-in water emulsion technique. The study of their optical properties demonstrates their ability to support Mie resonances in the visible. These resonances are associated with the excitation of a magnetic dipole, which constitutes a prerequisite to the realization of metamaterials with negative permeability.

J. Dintinger and T. Scharf, *Proc. SPIE 8269*, 82691C (2012).

Broad band tuning of the plasmonic resonance of gold nanoparticles hosted in serlf-organized soft materials. The extraordinary properties of reconfigurable soft materials are used to drive the resonance properties of noble metal nanoparticles, using an approach that puts a bridge between soft matter and plasmonics. Gold nanoparticles have been dissolved in a cholesteric liquid crystal and then infiltrated in a micro-periodic polymeric structure, realized by combining a holographic step and a microfluidic etching process. The spectral behavior of the nano-composite soft-structure has been investigated in the UV-Vis range for two different polarization directions of the impinging probe light. Correlation between the optical response and external perturbations (electric field, temperature variation) gives an outstanding example of broadband tuning of an “active” plasmon resonance.

L. De Sio, R. Caputo, U. Cataldi, and C. Umeton, *J. Mat. Chem.*, 21, 18967-18970 (2011).

Universal Soft Matter Template for Photonic Application. A new class of high efficiency photonic devices can be realized by combining the optical properties of anisotropic, soft, composite materials with re-configurability, owing to a specific confining geometry and to high response properties. A light sculptured polymeric template is used to micro/nanoconfine a wide selection of organic elements, stabilized through self-organization processes at the nanoscale. We exploit a general purpose method, used to align several kinds of liquid crystalline materials: an excursus of well known optical, electro-optical and all-optical effects is reported, which confirms the capability of our polymeric template to induce self-organization, without the need of any kind of surface chemistry.

L. De Sio, S. Ferjani, G. Strangi, C. Umeton, and R. Bartolino, *Soft Matter*, 7, 3739 (2011).

Metallic subentities embedded in micro-periodic composite structure. We report on the fabrication and characterization of a micro periodic structure realized in soft-composite materials containing metallic nanoparticles. The particles are used to infiltrate a passive polymer template realized by combining a holographic curing setup and a microfluidic etching process. In other experiments, small amounts of nanoparticles are dissolved in the original mixture utilized for the realization of polymer-liquid-crystal-polymer-slices gratings (POLICRYPS); this enables to fabricate POLICRYPS-like structures showing novel electromagnetic properties. Obtained structures are characterized in term of impinging probe polarization in the UV/visible range. Correlation between the optical response and external perturbations (electric field, temperature) is also reported. These first attempts are oriented to the fabrication of devices with tunable metamaterial properties.

L. De Sio, R. Caputo, U. Cataldi, J. Dintinger, H. Sellame, T. Scharf, C. Umeton, *Proc. SPIE 8114*, 81140I (2011).

Universal soft matter template: from photonic to metamaterial applications. We report on the realization and characterization of a polymeric template sculptured in photosensitive material, on a chemical inert surface. The structure is devoted to micro/nanoconfinement and stabilization of a wide range of organic and nano-particle components with selfarrangement properties at the nanoscale. High quality morphology of a polymeric, micropatterned, array is obtained by combining a, nano-precision level, optical holographic setup and a multi-step chemico-physical process. The "universal" template represents the basic platform to be filled with different organic materials, which can also include metallic nano-particles. The long range self-organization is induced without making use of any kind of surface chemistry. Due to their capability of exhibiting self organization, light responsive Liquid Crystals (LC) and short pitch Cholesterics LC have been exploited, and experimental studies have been carried out in order to investigate the photo-optical and elecro-optical response of obtained composite structures for the realization of photonic devices. Finally, the possibility of including metallic nano-particles has been also investigated, with the aim of inducing a "metamaterial" behavior of the realized structure.

C. Umeton, L. De Sio, R. Caputo, S. Ferjani, G. Strangi, and R. Bartolino, *Proc. SPIE 8114*, 81140W (2011).