Nanogold Project publishable summary

1. Summary description of project context and objectives

Composite materials incorporating organic and inorganic components are important in many fields of technology. Within the “Nanogold” project we study self-organization, morphology, and optical properties of composites to be used as next generation optical materials. The basic idea of our concept is to use electromagnetic resonances on different scales to achieve new electromagnetic properties. Our concept is based on the use of small metallic nanoparticles forming clusters and made in films to serve as three dimensional metamaterials. In the first year, we verified the theoretical feasibility of our model. Several techniques were developed to fabricate thin films containing resonant metal nanoparticles. We developed recipes for layer-by-layer assemblies, surface metal nanoparticle cluster materials and optical device fabrication by templating and with high nanoparticle loads. New self-organizing composite materials were synthesised and will be used as base material for further investigations. Having methods for fabricating multidimensional composite structures at hand, we aim further to design first functional structures, simulate their optical properties, realize them, and use advanced spectral characterization techniques to proof their nonconventional electromagnetic response.

http://nanogold.epfl.ch/

Metamaterial design with resonant nanoparticle

Only few electromagnetic design proposals for metamaterials exist that are adapted to self-organization and which relies in their fabrication on organic materials and metallic nanoparticles. Such designs should be robust enough to allow random arrangement of resonant entities in the long range order, as it is most often found in volume fabrication processes, but it should comprise at least a well-defined short range order to induce desired resonances in a well defined frequency domain. Organization of entities with nanometer precision, although possible on monolayer surface films, is yet a challenging problem in three dimensions. To obtain the necessary resonances of the electric and magnetic fields we suggest structuring at different length-scales. Key features of the design are dense nanoparticle self-assemblies or clusters with high volume fraction of nanoparticles (>30%) which have to have a size above 5 nm to induce plasmonic resonances at sufficient strength and low damping. The nanoassemblies/clusters have sizes between 50 and 250 nm and should be preferentially arranged in more or less regular structure. With that we can assure that their size tends to be yet sufficient small when compared to the wavelength of operation such that if they are densely arranged in space, the propagating light will not resolve the fine details of the structure but rather probes for an effective medium. The properties of this effective medium are dictated by the peculiar scattering properties of the nanoassemblies/clusters. Therefore, their exploration is at the heart of this project.

Resonant nanoparticle arrangements in organic materials

An interesting approach is to design and synthesise an entire material that is a composite and contains resonant entities, i.e. metallic nanoparticles. One possible material class relies on organic molecules incorporating inorganic particles. A regular arrangement of nanoparticles is preferred since it assured the required high volume filling fraction and a possible route to achieve this is self-organization. By anticipating that the substance is not a mixture, self-organization has to start at the molecular level and the molecules have to be arranged with long range order. Mainly chains of nanoparticles are formed that show long range and bond order. Accessible geometrical arrangements and structures are shown in Figure 1 and depend on the alignment of the liquid crystal molecules.

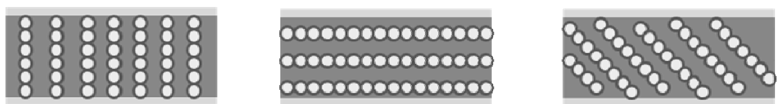

Figure 1: Orientations found if chains of nanoparticles are observed in smectic liquid crystalline phases.

The main problems with such materials are the high viscosity, which makes it difficult to have large domain formation, and the preparation of uniform samples across larger areas. Usually, processing can be done at elevated temperatures which require stable compounds that do not decompose. Available materials are still too experimental but a proof of principle was done for small particles with approximately 2 nm in diameter that support already the required resonances, though at an insufficient strength. We work on routes to design substances that can be processed, have a larger variety of phases and particle arrangements and therefore attract more interest for electromagnetic materials design.

Fabrication of complex structure containing dense nanoparticle arrangements

Complex assemblies of nanoparticles in matrices can be achieved by using polymers and self-assembly together with wafer processing technology. In such a hybrid approach the structuring on different length scales is accessible. Most of the metamaterial designs are based on dense particles arrangements. Particles arranged in layers might lead already 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 2.

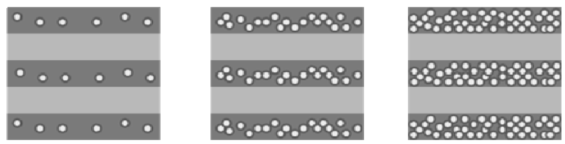

Figure 2: Possible structures realized with different techniques. The bright spots represent resonant nanoparticles that are arranged in layers. For phase separation techniques the mixing and wetting behaviour is the main issue.

We develop recipes to achieve dense particles assemblies in multilayers. Of special interest are systems that allow structure built up with particular nanoassemblies. In such a nanoassembly or cluster, a large number of nanoparticles form an entity. Such nanoassemblies can have special combined electromagnetic resonance properties and they are often called metaatoms. Material compositions that can be imagined and which are accessible to the consortium are shown in Figure 3. A typical diameter of nanoassemblies is 200 nm and distances should reach close packing for an efficient metamaterial formation. This requirement derives from the desire to induce strong dispersion in the effective properties. Nanoparticles incorporated into such nanoassemblies have diameters below 50 nm. Realization of such structures can be envisaged with a multitude of techniques. An important fact is that effective electromagnetic scattering and resonance properties are only achieved when the density of resonance units or nanoparticles is high.

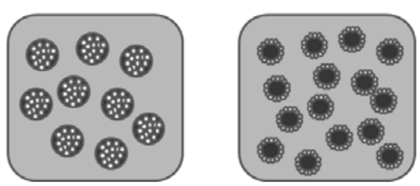

Figure 3: Possible structures realized with different techniques. The main problem for phase separation techniques is the mixing and wetting behaviour. The small bright dots represent metallic nanoparticles, which could be packed in nanoassemblies or at an interface of inclusions.

In our project we investigate ways to make nanoassemblies/metaatoms with physical chemistry of functionalized nanoparticles, and we develop strategies creating bulk materials by mixing and phase separating different materials such as liquid crystals and polymers to achieve high nanoparticle concentration.

2. Description of the work performed since the beginning of the project and the main results achieved so far

Nanogold derives its novelty from the idea of using self-organization to implement structure at different lengths scales and combine this with resonance effects. The material class we are looking is mainly formed from amorphous assemblies of nanoparticle clusters. We use nanoparticles that have resonances. Combining them in clusters allows tuning the resonance frequency and strengths. To assemble such clusters to bulk metamaterials is the final aim. In the first half of the project, foundations are laid to device fabrication. Intensive research on amorphous metamaterial designs based on nanoparticles was started and simulation tools for plasmonic materials structured at different scales were established. A toolbox for plasmonic nanomaterial fabrication was established that is based on self assembling materials, physical chemistry techniques for structure formation and templating. Liquid crystal based self-assembled plasmonic materials containing plasmonic entities with sizes larger than 4 nm were synthesised. Structures of highly order liquid crystal phases containing smaller nanoparticles were investigated and successfully described. Unusual structural transitions were found in such materials. Due to a moderate density of plasmonic entities, which weakened the induced dispersion, the optical properties of the actual materials were yet dominated by the organic host material. Important changes of the materials permeability's are expected for larger plasmonic entities of a second generation material. To engineer more actively the density of plasmonic entities meta-atoms and meta-layers built from nanoparticles assemblies were fabricated. Our approach here was electrochemistry that allows deposition of amorphous multilayer of nanoparticles of nearly any size. We have chosen effective plasmonic entities and assemble three dimensional structures starting from a layer built up approach. We showed that in such structures magnetic dipole moments can be measured and went on to more complex systems. The minimum distance of plasmonic particles assembled with electrochemistry is given by the electrostatic interaction of wrapping molecules. To have highest density nanoparticles a particular cluster material was produced based on high density nanoparticle inks. With such a material, clusters of different size and shape can be produced and stabilized without losing the resonance behaviour. Plasmonic resonance and interference as well as scattering are the basic operational principles that, combined in the right manner, can lead to unusual electromagnetic behaviour. We achieved to make a bulk amorphous cluster layer material that shows plasmonic resonances and interference of light, a first step to bulk metamaterial properties.

To assure the use of such materials in devices, certain functionalities have to be demonstrated. Among others we consider waveguide devices. Technology compatibility of holographic written structures with plasmonic material was approved and will allow us fabrication of first test devices with unusual response based on dense plasmonic cluster materials.

3. Description of the expected final results and their potential impacts and use (including socio-economic impact and the wider societal implications of the project so far)

The importance of metamaterial research is shown in the number of initiatives to stimulate the research and is out of question. Despite the impact of the photonic metamaterials for a lot of applications, in general, our approach adds particular advantages not accessible by using conventional or advanced nanotechnology. Five impact areas can be reached with our approach of a self-assembled composite metamaterial.

1. Physics and technology of metamaterials
2. Chemistry of nano-composite material
3. Engineering of composite materials for sensing and optics (sensing, photonics, resolution, decoration…)
4. Technology of liquid crystal devices with macromolecules
5. Management of thermal radiation at the nanoscale

Our project is the first bottom up approach for metamaterial fabrication and boosts technology development in the field. A lot of designs today are based on restrictions given by means of nanotechnology fabrication.

Chemistry of nano-composites is a wide field of research. First applications of self organized composite materials with thermotropic properties will lead to a rush to this material class. The concept can be widened to allow specific material design for applications like sensing paints. One aspect of materials characterization like macromolecular assemblies is the development of low-resolution crystallography methods for determination of nanostructures of self-assembled metamaterials. This is in so far important as the structures dimension does not fit well with classical structural analysis means.

Until now engineering of nano- and microstructure composite materials in the context of optical functionality is rare. Moulding and film processing as well as fibre spinning are used to bring materials into shapes. Bulk materials can be shaped very precisely. If one considers high resolution of spatial modulated materials only very few results are available that show optical functionality. The main problem today are clustering of nanoparticles, de-mixing and wetting problems. Our material concept is explicitly based on such effects and our material designs will contribute largely to apply fabrication concepts available in this area. In a long run, when materials are designed that can be processed at room temperatures; the whole plastic technology process chain including injection moulding and hot embossing will be available for fabrication. Additionally it is expected that the material has highly anisotropic electrical conductivity. Such properties can impact device development for organic electronics and solar cells.

One possible short term application of a metamaterial consisting of plasmonic nanoparticles can be on the emission of thermal radiation. As it was predicted theoretically, thick slabs of ordered layers of gold nanoparticles exhibit an emission spectrum which is suppressed in the infrared regime and enhanced above a certain cut-off frequency in the optical regime. Such structures are ideally suited for incandescent light bulbs: the thermal energy provided by heating the metamaterial is transformed into thermal radiation mostly in the visible regime leading to much increased energy efficiency.