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Bio-Synthetic Electromagnetic Metamaterials

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Abstract

Metamaterials have a number of novel physical phenomena, such as a negative index of refraction, inverse Cherenkov radiation, inverse Doppler shift and the ability to engineer the dispersion. If successfully manufactured they, would in turn, offer the possibility of fabrication of a range of novel technologies.

One of the key factors limiting metamaterial development is the need to develop fabrication techniques capable of high-fidelity mass fabrication of nanostructures. In this paper we consider beating this limitation by using biological systems as "foundries" for the anthropogenic construction of nanostructured materials. Using DNA origami as a scaffold structure it is possible to rationally direct site specific, or global, metallization, of 3D structures on the nanoscale. This paper will demonstrate our strategy to create novel negative index of refraction metamaterials in the visible and infrared part of the EM spectrum.

1. Introduction

In recent years growing research into the area of metamaterials has shown these materials offer great promise in numerous applications, ranging from strip lines to antennas. Metamaterials allow microwave designers to obtain electromagnetic characteristics not typically available in nature, leading to new behaviour, as well as reductions in the size of typical devices. The origin of metamaterials predates the 19th century, and the history has been reviewed in several books, for example reference [1].

Metamaterials consist of a number of, periodic, sub-wavelength structures whose characteristic properties are determined by their subwavelength geometry rather than their material composition. This results in the collective system behaving in a homogeneous manner over certain wavelengths/frequencies of interest (adhering to the effective medium condition) allowing the use of the abstract bulk properties of permittivity (ε) and permeability (μ), defined from the constitutive relations,

$$\begin{aligned} \boldsymbol{D}(\boldsymbol{k},\boldsymbol{\omega}) &= \boldsymbol{\varepsilon}(\boldsymbol{k},\boldsymbol{\omega})\boldsymbol{E}(\boldsymbol{k},\boldsymbol{\omega}) \\ \boldsymbol{B}(\boldsymbol{k},\boldsymbol{\omega}) &= \boldsymbol{\mu}(\boldsymbol{k},\boldsymbol{\omega})\boldsymbol{H}(\boldsymbol{k},\boldsymbol{\omega}) \end{aligned} \qquad (1)$$

Where the permittivity (ε) and the permeability (μ) are the averaged response functions of the molecules in the material to the incident electric and magnetic parts of the EM wave incident on to the material. The metamaterials discussed here (following the Walser definition [1]) refer to both ε and μ being simultaneously negative at a specific wavelength range. The first systematic theoretical study of simultaneously negative ε and μ materials was undertaken in 1968 by Veselago [2]. Who showed that for a monochromatic uniform plane wave in such a medium the direction of the Poynting vector is antiparallel to the direction of the phase velocity. Veselago also noted that such a medium would have a negative index of refraction and presented the possibility and behaviour of a lens constructed from this material.

The 1999 seminal paper by Pendry [3] marks a turning point in the research of metamaterials, presenting the key sub-wavelength elements that form the metamaterial unit-cell (artificial atom), the Split Ring Resonator (SRR) and wire array [3]. The SRR remains the meta-atom of choice for many researchers, especially at sub-THz frequencies, and is the main focus of our study in this paper. At the scale of an individual SRR the incident EM wave produces a magnetic flux opposing the incident field. The split in the ring prevents the current circulating, creating a capacitance, forming an equivalent LCR circuit. The size of our SRR meta-atom is much smaller than the wavelength of incident EM allowing for a system composed of many SRRs to be treated as a "homogenised" media described by an effective medium approach [1]. Where the effective permittivity and permeability are found in terms of the permittivities, permeabilities and geometry of the individual constituents of the system. By manipulating the specific geometry of the unit-cells we can engineer the dispersion relation of the material to exhibit novel electromagnetic properties, such as engineering an arbitrary phase shift of an incident EM wave.

The key to the design and operation of a metamaterial is to precisely fabricate the sub-wavelength unit cell geometry. As a general guideline to use an effective media model for our material we require the SRR geometries to be less than λ/10 in size.

At MHz frequencies standard CnC and PCB lithography can be used to for the unit-cell geometries, but for higher frequency feature size and speed of fabrication throughput become an issue.

Over the last few decades, extensive research has been undertaken into developing techniques for the fabrication of semiconducting/metallic nanostructures with top down design methodology. These approaches have been limited by their inability to deliver, high-fidelity, mass-production with feature size smaller than 20nm. Currently the state-of-the-art in fabrication of nanometamaterials is limited to the production of a sample 16μm x 16μm, consisting of an array of SRRs, each of size 480nm [5]. For metamaterials research to evolve the field requires a reduction in component size coupled with a higher production rate and the introduction of truly 3D nanoscale fabrication.

The key aim of our paper is to explore the use of biological systems foundries to fabricate sub-wavelength, metallic, nanostructures to form novel EM materials. In biology there are many examples of organisms that synthesize organic-inorganic composite materials for support and protection, using DNA to position atoms with atomic precision across scales from <10 nm to >10m. Specifically we explore the application of DNA origami to engineer 2D and 3D nanoscale shapes by the specific folding of DNA.

Section 2 of this paper presents the background of DNA origami. Section 2.2 examines the structure we propose to fabricate and study, with section 3 exploring the EM response and categorisation of this material.

2. DNA origami

DNA origami is a technique pioneered by Rothemund [5] as a methodology to fold DNA strands into rationally designed arbitrary shapes. Forming structures around 100nm in total size with features below 10 nm. Using single long strands mixed with a series of complementary strands called staples. The approach exploits the highly predictable Watson-Crick base pairing and the unique mechanical properties of DNA to engineer a set of sequences that when annealed form novel predetermined structures.

The rational of DNA origami design is to utilise a single long DNA strand ‘scaffold’, (A single strand of ~7 kilobases) where staples are added, which conform connecting helices, creating “Holiday” junctions between strands to form the scaffold into the desired shape[5]. Each staple is defined as set of nucleotides corresponding to the complementing sequences to their position on the scaffold sequence.

As a construction method based on the rational self-assembly of organic molecules this bottom up process offers a very high throughput. Facilitated by our understanding of both artificially synthesising and replicating large quantities of novel sequences very quickly, [6] while also providing high yield and higher purity, this approach has benefits over systems which rely purely on smaller sequences of DNA as small sequences are very sensitive to relative stoichiometry. Difference in the ratio of strands can lead to a high percentage of misfolded structures or anomalous aggregation of small sequences [5].

To facilitate curvature in structures the use of the mechanical properties of both individual helices and the Holliday junctions between them to generate stress can be used to predictably and reproducibly create bend and curve. Working upon the premise that in its native B form conformation a DNA helix has a helical pitch of 360 degrees every 10.5 base pairs. If 2 helices in proximity are connected via Holliday junctions and insertions or deletions lead to a mismatch in overall length between relative Holliday crossovers the shorter strand will exert mechanical stress on the longer strand causing it to curve.

Given the nature of DNA replication and formation once a specific sequence has been derived, the fabrication process can be repeated with ease on a massive scale.

2.1 Metalisation

To enable the interaction of the DNA nanostructures with an incident EM wave part, if not all, of the DNA scaffold needs to metalised. There are many potential strategies for metalisation of DNA origami constructs. Broadly speaking they can be divided into 2 categories: Those which allow rational addition in topological terms where metal particles will bind specifically to a chosen sequence [6] and those which cause aggregation in a global manner due to specific properties of DNA [7]. The aggregation root to metalisation occurs by a seeding step [7] in which the DNA structure is exposed to positively charged amine groups, which bond to the electronegative phosphodiester DNA backbone, and are bound to gold nanoparticles. A further growth step [7], where elemental gold ions are exposed to the seeded DNA origami, in which length of exposure defines the levels of aggregation of gold to the structure, facilitates total metalisation of the DNA origami fabrication.

2.2 Proposed SRR

While scaffold fabrication allowed simple rationalisation of pixelated 2D designs, greater design considerations, specifically the leap from 2 to 3 dimensional constructs required a higher level of computational aid [8]. The package we used here is caDNAno [10] and allows a rectangular honeycomb/square grid orientation of helices to be defined both in terms of individual sequence and interactions via Holliday junctions [8].

The base design goal was to achieve a SRR with 100nm outer radius, 90nm inner radius and 157nm split. Using caDNAno we designed a structure consisting of 6 long strand DNA scaffolds, as shown in Figure 1. The scaffold strands are selected for suitability in size and complementary sequences given to each *in situ* staple. The staple strand length is 30-50 bases to increase stoichiometric similarity between individual synthesised sequences promoting correct folding and creation of a monomeric species in the recovered folding reaction product [9].

The caDNAno simulations were repeated iteratively to find the correct topology to form the required SRR. These simulations determined the correct lengths and bases in each DNA scaffold. Scaffold-0 490 base pairs, scaffolds-1/3 473 base pairs, scaffolds-2/4 441 base pairs, scaffolds-5 422 base pairs. Where these dimensions take into account the effect of metalisation of the DNA scaffold needed to create the final SRR. The staples are configured in such a way that the mechanical forces between scaffolds pull the DNA bar into a C-shape forming an individual SRR. Cando [10] simulations are used to determine if the final design will conform to the chosen dimensions and it is useful to run simulations where changes are made and then checked in a continuous cycle. Having determined the base pair configuration required to generate the SRR configuration, we use a commercial synthesis service to purchase a custom 96-well oligonucleotide using oligo sequences determined by caDNAno.

3. EM Material parameters

To predict and characterise the EM response of a metamaterial fabricated from the above structure we model an infinite sheet of metamaterial using HFSS. HFSS is a commercial finite element method solver for electromagnetic structures from Ansys. We simulate the infinite sheet by modelling an individual unit cell of the above SRR geometry. HFSS models the unit cell shown in figure 3, where the SRR is modelled as a Perfect Electrical Conductor, using Bloch-Floquet boundary conditions to create the infinite sheet. Where the HFSS simulations [11] focus on modelling the frequency domain to determine the S-parameters.

We determine the effective permittivity and permeability from measurements of the scattering parameters (S-parameters). Using a variant of the Nicolson-Ross-Weir NRW approached adapted by Smith [12] to account for possible negative responses in the real components of the permittivity and permeability.

The NRW uses a closed form expression allowing the complex form of the permittivity and permeability to be determined directly from S-parameter measurements. In addition the NRW technique is relatively robust to experimental error. Assuming the material is a free-standing slab (thickness d) surrounded by a vacuum, with normal incident plane waves, then the free space wave vector, $Z=Z'+iZ''$ the impedance of the material, and $n=n'+n''$ the refractive index are given by;

$$Z = \pm\left[\frac{(1+S_{11})^2-S_{21}^2}{(1-S_{11})^2-S_{21}^2}\right]^{1/2} \tag{2}$$

$$n' = \pm\frac{1}{kd}\Re\left[cos^{-1}\left(\frac{1-S_{11}^2+S_{21}^2}{2S_{11}^2}\right)\right] + \frac{2\pi m}{kd} \tag{3}$$

$$n'' = \pm\frac{1}{kd}\Im\left[cos^{-1}\left(\frac{1-S_{11}^2+S_{21}^2}{2S_{11}^2}\right)\right] \tag{4}$$

$k=2\pi/\lambda_0$ is the free space wave vector, the permittivity and permeability can be found directly, $\varepsilon_{eff} = n/Z$ and $\mu_{eff} = nZ$. The complication of course is in choosing the root and branch of the above equations. For a passive media the imaginary components of ε_{eff}, μ_{eff}, n and the real component Z must be positive (except at points of anti-resonances). The inverse cosine introduces some ambiguity into the imaginary component of n. To constrain the solution, we ensure that n' is continuous across the frequency range. This approach has been demonstrated repeatedly to correctly give the permittivity and permeability for both conventional materials and metamaterials [1].

Figures 4-7 present the numerical results from the HFSS simulations, showing S_{11} and S_{21} over the frequency regime that corresponds from the near infrared to blue optical regime of the EM spectrum. Using equations 2,3 and 4 the impedance, permittivity, permeability and Absorption are determined and shown. It is of note that over the whole optical regime the

metamaterial is predicted to have simultaneous negative permittivity and permeability, giving a negative refractive index. Whilst the absorption coefficient is relatively high in the blue part of the spectrum after the impedance becomes reactance dominated the absorption coefficient decreases, although is still relatively high.

7. References

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