A combinatorial approach to metamaterials discovery

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Abstract
We report a high throughput combinatorial approach to photonic metamaterial optimization. The new approach is based on parallel synthesis and subsequent optical characterization of large numbers of spatially addressable nanofabricated metamaterial samples (libraries) with quasi-continuous variation of design parameters under real manufacturing conditions. We illustrate this method for Fano-resonance plasmonic nanostructures, arriving at explicit recipes for high quality factors needed for switching and sensing applications.

Keywords: metamaterials, combinatorial engineering, Fano resonance

(Some figures in this article are in colour only in the electronic version)

Some fifteen years ago a paper reporting a combinatorial approach to materials discoveries revolutionized materials research and other disciplines such as chemistry and pharmacology by demonstrating a method for high throughput parallel synthesis and analysis of novel artificial chemical compounds [1, 2]. Here we report the first application of the combinatorial approach to discovery and optimization of photonic metamaterials. Metamaterials are manmade media with all sorts of unusual functionalities resulting from sub-wavelength structuring. We apply the combinatorial approach to the optimization of an important class of photonic metamaterials supporting Fano resonances [3] that recently became prime platforms for new switching, gain and sensing applications, and slow light and polarization control devices (see review [4]). These metamaterials are arrays of asymmetric split ring metallic wire resonators or complementary arrays of ring slits in a metal film. Their application potential depends on the presence and characteristics of reflection and transmission peaks associated with a particular mode of electromagnetic excitation that is weakly coupled to free-space (closed or trapped mode). The characteristics of this resonance are very sensitive to the structure’s environment and are responsive to its changes making them a prime choice for active metamaterial applications. These resonances can be tailored by design: their spectral position, width and depth depend on many parameters, most notably on the metal used for their fabrication, the ring’s size and the characteristics of the split [5–7]. Optimization of the resonance characteristics of these metamaterial structures is relatively straightforward in the microwave and terahertz parts of the spectrum using numerical electromagnetic modeling tools. For the optical spectral range, which requires nanostructured meta-molecules, optimization by numerical modeling becomes considerably less reliable for two reasons. First, accurate reproduction of the idealized design parameters is not possible due to limitations of the nanofabrication technologies, in particular sharp edges and ideal vertical cuts are not achievable when the metal surface roughness is comparable to the smallest design features. Second, the electromagnetic material properties used in calculations, in particular those of nanostructured metals are not known to the necessary accuracy and are normally replaced by those of bulk media. However, they can differ significantly from those of bulk metals due to the higher role of surface electron and defect scattering in granulated and nanostructured metals. The unsatisfactory character of this substitution is well recognized by the metamaterials research community, where in some calculations adjusted bulk dielectric parameters are used...
for nanostructured metals to achieve a better fit to experimental data.

The combinatorial approach presented below aims to address the difficulty of optimizing photonic metamaterial designs through computer modeling by resorting to parallel synthesis and subsequent optical characterization of a large number of spatially addressable nanofabricated metamaterial samples (libraries, see figure 1(a)) with quasi-continuous variation of the design parameters. Both sample library fabrication and characterization may be automated, providing a potentially high throughput screening method. We also compare the results of combinatorial optimization with those of numerical modeling.

We studied metamaterials consisting of arrays of square split ring aperture meta-molecules in the field of parameters defined by the unit cell size and the split’s asymmetry (see figure 1(b)). Here $s \times s$ is the overall size of the square unit cell while in all cases the split ring aperture’s outer and inner sides $a$ and $l$ are 100 and 200 nm smaller than $s$, respectively. The design slit width $w$ was 50 nm and the parameters $t$ and $b$ define the split’s asymmetry and size. Two libraries of regular $30 \times 30 \ \mu m^2$ arrays of split ring apertures in a 30 nm thick layer of gold were fabricated by electron beam lithography on a glass wafer. In both libraries the unit cell size $s$ was varied from 400 to 500 nm in 25 nm steps. In library A parameter $b = 0$ was fixed and a gap size asymmetry $\alpha = t/l$ ranging from 0.1 to 0.7 in steps of 0.1 was introduced. In library B the gap size was fixed at 0.3$\mu$m and a gap position asymmetry $\beta = (t - b)/(t + b)$ ranging from 0 to 1 in steps of 1/7 was introduced.

The transmission and reflection characteristics of these photonic metamaterials were measured in the 800–2000 nm spectral range for waves polarized parallel to $t$ using a microspectrophotometer. These properties were also simulated with a full three-dimensional Maxwell finite element method solver in the frequency domain using the Drude model for the dielectric constant of gold [8].

For a fixed meta-molecule size of $s = 500$ nm, the metamaterial’s transmission, reflection

Figure 1. (a) Schematic of a combinatorial library. (b) Schematic of the metamaterial unit cell. (c)–(d) Scanning electron micrographs of meta-molecules with small and large gap position asymmetries, $\beta = 1/7$ and 1. (e) Characteristic I symmetric (anti-bonding) and II–III antisymmetric (bonding) modes of excitation associated with the absorption resonances for $\beta = 1/7$ and 1. Excitation wavelengths: 820, 1025 and 1200 nm, respectively.

Figure 2. Library A—gap size asymmetry $\alpha = t/l$, where $l = s - 200$ nm and $b = 0$. (a) Transmission, (b) reflection and (c) absorption spectra as a function of asymmetry breaking $\alpha$ for unit cell size $s = 500$ nm. The dashed line marks the absorption maximum. (d) Combinatorial maps of resonance sharpness FOM as a function of $s$ versus $\alpha$. (FOM = $\lambda_0/\Delta \lambda$, where $\lambda_0$ and $\Delta \lambda$ are the wavelength and FWHM of the absorption resonance.) Note that the experiments (top) cover a slightly smaller asymmetry range than the simulations (bottom) and that the data have been interpolated in between manufactured samples.
and absorption properties depend on the gap size asymmetry \( \alpha = t/b \) when \( b = 0 \). In the symmetric case the metamaterial has broad reflection and transmission maxima around 800 nm and 1400 nm respectively, while the absorption spectrum is featureless. Symmetry breaking, \( \alpha > 0 \), leads to the appearance of a Fano resonance: the broad reflection maximum is split by a narrow resonant reflection minimum appearing at about 900 nm (see 2(b)) which is associated with a narrow absorption peak marked by a dashed line (see 2(c)). Furthermore, at slightly shorter wavelengths, a transparency window opens up, which may be discussed in terms of electromagnetically induced transparency [9]. Larger symmetry breaking leads to broadening of the absorption resonance, which red-shifts due to the increasing size of the top aperture.

Figures 3(a)–(c) show how the metamaterial transmission, reflection and absorption depend on the gap position asymmetry \( \beta = (t - b)/(t + b) \) for \( s = 500 \) nm unit cells with a 90 nm gap. Similarly to the gap size asymmetry, a gap position asymmetry \( \beta > 0 \) leads to the appearance of a Fano resonance at 1000 nm, which can be seen as a narrow splitting of the broad reflection maximum of the symmetric structure (see 3(b)). The Fano resonance is associated with an absorption peak marked by a dashed line (see 3(c)) and broadens and red-shifts with increasing asymmetry. Intriguingly, simulations reveal an additional narrow absorption resonance at 830 nm, which should be supported by the symmetric structure and which slightly blue-shifts and ultimately vanishes with increasing asymmetry \( \beta \), see figure 3(c). The fundamentally different nature of these resonances is revealed by the associated modes of excitation—compare the modes in figure 1(e) with the resonances marked in figure 3(c). The symmetric structure supports a symmetric mode I, where the top and bottom apertures interact through in-phase magnetic fields. Symmetry breaking allows the excitation of an antisymmetric mode II, where the apertures of each ring interact through anti-phase magnetic fields. These modes can be understood as the hybrid modes of two coupled resonators (apertures), I being the higher energy anti-bonding and II being the lower energy bonding mode [10].

Increasing symmetry breaking the bonding mode II becomes dominated by the longer aperture, see III. We note that I–III are higher order modes of the split ring aperture system, while the broad transmission band at 1400–2000 nm corresponds to a lower order resonance of the shorter slit [7].

As discussed in the introductory paragraph, narrow Fano resonances have a wide range of applications. To quantify the width of the bonding resonance we introduce a figure of merit, \( \text{FOM} = \lambda_0/\Delta \lambda \), where \( \lambda_0 \) and \( \Delta \lambda \) are the wavelength and full width at half maximum (FWHM) of the absorption peak. As illustrated by figures 2(d) and 3(d), for both types of symmetry breaking smaller asymmetries lead to narrower Fano resonances, while the resonance width is remarkably insensitive to the meta-molecule size, which controls the resonance’s spectral position.

As illustrated by figures 2 and 3, the numerical results and experiments show similar qualitative behavior, indicating that simulations do provide useful guidance for the design and understanding of photonic metamaterials. However, quantitative comparison shows substantial differences.

In particular, the spectral positions of the measured absorption resonances are about 80 nm red-shifted relative to the simulation results. This shift may be explained by the uncertain real part of the dielectric constant of nanostructured gold at optical frequencies. Also systematic manufacturing inaccuracies like the inability to fabricate sharp corners at the nanoscale contribute to a spectral shift of resonances, see figures 1(c)–(d). In general, the spectral positions of Fano resonances in plasmonic metamaterials are also extremely sensitive to thin cover layers, or layers of oxides or contamination, as has recently been demonstrated by a three-fold metamaterial transmission increase resulting from application of a single graphene layer [11].

While simulations predict remarkably narrow resonances of up to FOM = 50 for small asymmetries around 0.1, the experimentally observed resonances are broadened, FOM \( \leq 12 \), and weakened so much that they cannot be clearly identified for asymmetries \( \alpha \leq 0.3 \) and \( \beta \leq 3/7 \). Small size variations and manufacturing tolerances in reproducing a perfect square array of meta-molecules [12], rough gold
surfaces as well as finite array sizes [13] were shown to lead to resonance broadening and weakening in real structures, while these factors are not accounted for in simulations of infinite arrays of identical, ideally smooth meta-molecules. Additionally, the resonance widths strongly depend on the imaginary part of the metal’s dielectric constant which controls losses in plasmonic nanostructures and may be larger than the commonly used literature values [8] for nanoscale gold volumes at optical frequencies due to increased electron scattering rates. These factors can also explain the high absorption background and the absence of the remarkably narrow anti-bonding resonance in our experiments.

For practical applications a trade-off between narrow Fano resonances (small asymmetry) and strong Fano resonances (large asymmetry) must be considered. The optimal design parameters will always depend on the accuracy of the available nanostructuring technology and can be found through the high throughput screening method demonstrated here. In our case asymmetries around $\alpha, \beta \approx 0.4–0.5$ yield strong and narrow resonances, making them the best choice for most sensor and switching applications, which is in stark contrast to simulations suggesting optimal asymmetries around 0.1.

In summary we report a high throughput combinatorial approach to the design and optimization of photonic metamaterials. We show for Fano resonances in split ring aperture arrays that the optimal metamaterial parameters can be found through parallel synthesis and characterization of material libraries with quasi-continuous variation of design parameters under real manufacturing conditions. Being unable to take the inevitable shortcomings of nanoscale manufacturing into account, simulations can only provide qualitative predictions of metamaterial properties at optical frequencies. Nevertheless simulations remain a key tool for understanding the underlying mechanisms behind metamaterial functionalities. Here we have identified in detail how the asymmetry of split ring apertures controls Fano resonances in photonic metamaterials, which are relevant to various applications ranging from sensing, switches and slow light devices to the ‘lasing spaser’ [14].

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