

Manuscript: NCOMMS-15-18423-T

Title: Highly Tunable Refractive Index Visible Light Metamaterials from Symmetry Control Block Copolymer Self-Assembly

Response to Reviewer's Comments

(Editorial comments in plain text, Author's comments in **bold blue letter**)

We appreciate all reviewers' careful and insightful comments. We revised our manuscript to incorporate these comments and below we provide our point-by-point response.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors fixed most of the previously raised points. Several minor issues should however be fixed before publication:

The title is not very appropriate: where does the "symmetry control block copolymer self-assembly" lie in the manuscript? The authors obviously imply the hexagonal order invoked by the self-assembly, but in which sense is there real control over symmetry? The authors only show one symmetry in the manuscript. I thus strongly suggest changing the title.

We appreciate this insightful comment. In this title, we indicate the 'symmetry control' by means of anisotropic shrinkage of the substrates rather than the intrinsic modification of pattern symmetry during block copolymer assembly process. Our post self-assembly approach indeed achieved the facile modification of pattern symmetry as shown in Figs. 4e & 4f. Overall, we demonstrate three different symmetries: C_{6v} , C_{4v} , and C_{2v} in the Schoenflies notation (Fig. 4). Nonetheless, we agree that the meaning of 'symmetry control' is unclear in the original title. In addition, we note that reviewer #3 also commented on our title. He/she suggest to modify 'metamaterial' into 'metasurface'. Taken together we changed our manuscript title as below.

"Highly Tunable Refractive Index Visible Light Metasurface from Block Copolymer Self-Assembly"

I terms of language some improvements are possible. For example "in its real part for visible spectrum" where "throughout the visible wavelength range" is probably more correct or "smaller than skin depth" rather than "smaller than the skin depth".

We appreciate this comment. The sentences were modified following reviewer's

comment.

Please add more recent literature on the refractive index of natural materials, see e.g. Leertouwer et al. Opt Exp 2011 and Yoshioka et al PRE 2011.

We appreciate this comment. We added the recommended references.

Missing word in abstract: "The effective REFRACTIVE index remains above.."

Missing word in introduction: "THE refractive index (in this work...)"

We appreciate this comment. The missing words were added in new version of manuscript.

Page 5: The large paragraph could be enhanced by adding a discussion on how percolation or higher topological structures could change the permittivity etc., especially in the light that many metamaterials have been produced by polymer self-assembly into an interconnected gyroidal morphology (Vignolini et al. 2011, Dolan et al. 2015).

We appreciate this constructive comment. We added these references and compared them to our system, at page 5.

Page 5: We note that interconnected structures can possess unusual optical properties rising from topology and polarization dependent resonances. On the other hand, the isolated metallic inclusions proposed here allow an easy control on the electric and magnetic responses over a broad frequency range in the long-wavelength regime.

Page 6: As a continuation of the argument above: polymer self-assembly can also induce COMPLEX shapes and not only "simple periodic configurations" the authors mention. There are in fact a multitude of complex morphologies (gyroid, diamond and other higher order genus-3-morphologies) that can be fabricated by block-copolymer self-assembly. This section should be changed accordingly.

We appreciate this comment. We agree that our wording was inaccurate. Therefore, we modified the corresponding part as below.

Page 6: The intrinsic geometric shapes accessible by BCP self-assembly include diverse and complex configurations, from hexagonal cylinder arrays and parallel line arrays to

double gyroids and other three-dimensional structures. Nonetheless, the topology is strongly correlated with the volume fractions of constitutive polymer blocks, governed by thermodynamics, and it is a huge challenge to vary the volume fractions by large amount while maintaining the desired topology.

Page 6: parameters, e.g. μ (on page 6) or d (on page 7), should be set in italic font.

We appreciate the reviewer's careful reading. All parameters are now set in italic font.

P.8, first paragraph: this relaxation mechanisms seems to be highly speculative. Please either add a cautious sentence or provide proof. In the context of this, the language of the authors is often quite "all-knowing": highlighting speculations and ideas could support the reader in understanding where the real problems and challenges still are.

We appreciate this comment. In the revised paragraph, we clearly differentiated our speculations from the facts that we observed with electron-beam and atomic-force microscopy.

Page 8: ... would be temporarily immobilized while the uncovered region as well as the bulk starts to shrink. We suspect that the resultant accumulation of inhomogeneous stress is the cause of the highly corrugated intermediate structure (Fig. 1c). The corrugation relaxes by a further heating process, during which Au nanoparticles might experience surface reconstruction owing to the enhanced mobility of Au at the elevated temperature (Supplementary Fig. 3)

P. 9: The authors added the imaginary part of the RI to the main text and the figure, however, the part of the main text could be polished a bit by two things: i) add values and ii) speculate as to why the RI is increasing so much. Can this be understood e.g. by Kramers-Kronig-theory?

We appreciate this insightful comment. We added the values of extinction coefficient in the main text and also commented on the relationship between the high imaginary part near the resonance and the high RI in the long wavelength regime (from K-K relationship).

As our system is subject to causality, the usual Kramers-Kronig relationship applies here as well, and the real part of the electric susceptibility (χ') is related to the imaginary part (χ'') via Hilbert transformation

$$\chi'(\omega) = \frac{2}{\pi} \text{P} \int_0^{\infty} \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2} d\omega'.$$

Now, assuming that the imaginary part is localized around several resonance frequencies ω_i , the value of the real part in the low frequency regime (much lower than any resonance frequency) is approximately

$$\chi'(\omega) \approx \frac{2}{\pi} \sum_i \omega_i^{-1} \int_{\omega_i - \delta\omega}^{\omega_i + \delta\omega} \chi''(\omega') d\omega'.$$

Hence, by introducing a new resonance with high imaginary part, one can increase the RI in the low frequency (long wavelength) regime.

Page 9: The imaginary part of the index, which is related to optical losses, exhibits a high peak value of 3.9 at 640 nm wavelength but becomes less than 0.5 at 840 nm and continues to decrease at longer wavelengths. (The high values of the imaginary part near the resonance wavelength are associated with the high values of the real part over broad bandwidth in the long wavelength regime via the Kramers-Kronig relationship.)

Overall, the paper is nearing publication quality, given the issues raised above.

Reviewer #2 (Remarks to the Author):

In this resubmission, Kim et al. provided faithful revision following reviewers' suggestions. The reviewer believes that the replies to the concerns raised by reviewers are proper, and the novelty of the manuscript in terms of the tunability, fabrication techniques, and isotropic nature still remains in the revised manuscript. The reviewer thus suggest the acceptance of this manuscript. For completeness, however, the reviewer suggest authors to add following discussions.

The main concern raised by all of the reviewers is focused on the impact of the obtained material values ($n + ik$). As the reviewer pointed out in the previous review, the obtained values or the figure-of-merit (n/k) are not far from ordinary semiconductors (Si or Ge), and may also be obtained from hyperbolic metamaterials (HMM) which can also satisfy the condition [$\text{TFSL} < d < \text{skin depth}$].

Of course, as commented in the previous review, the results from the authors show enough novelties proper to the standard of Nature Communications, in terms of demonstrated tunability compared to natural semiconductors and also isotropy compared to highly-anisotropic HMM.

In this regard, I suggest authors to provide little bit more expanded discussions on the impact of the manuscript, especially considering the applications of high refractive index structures [see e.g., Nano Today 10, 22-47 (2015); ref.4].

As well, since the result of ultrahigh-refractive index ($n \sim 5.5$) with bulk topological insulators in visible/IR ranges has been published recently in Science Advances [Yue et al. Sci. Adv. 2016; 2: e1501536]; using FIB for the application to solar cell devices, it is suggested to cite this paper with a proper discussion / comparisons (e.g., in terms of fabrication, or other characteristics).

We thank the reviewer for this suggestion. We added these references and discussed them in the revised manuscript.

Page 3: Materials with a high and controllable refractive index are crucial for diverse optical devices ranging from high-resolution imaging/lithography to optical communication systems, light management for optoelectronic devices.

Page 10: ... except several semiconductor materials such as Si and GaAs. Recently reported topological insulators possess even higher index approaching 5.5 in this wavelength range (Ref. Sci. Adv. 2, e1501536 (2016)), but the extinction coefficient is also quite high at near 2 or higher.

Reviewer #3 (Remarks to the Author):

The manuscript "Highly Tunable Refractive Index Visible Light Metamaterials from Symmetry Control Block Copolymer Self-Assembly" presents a self-assembly approach to fabricate a "visible light metamaterials" using block copolymer.

The results are novel. The experimental data regarding the sample fabrication and characterization are convincing.

The new version of the manuscript is greatly improved and the explanation of the imaginary part of the refractive index is now clear.

However, I still think that the title is still misleading, and the fabricated sample it is a meta-surface not a metamaterial.

We appreciate this comment. We note that reviewer #1 suggested to delete the phrase of ‘symmetry control’ in the title. Accordingly, we modified the title as below.

“Highly Tunable Refractive Index Visible Light Metasurface from Block Copolymer Self-Assembly”

Author requested in the rebuttal reference reporting record value of refractive index, here as an example, using plasmonic structure they reports refractive indexes larger than 100! (<http://pubs.acs.org/doi/abs/10.1021/nn5064198>). I suggest rephrase the paragraph.

We appreciate this suggestion. We now added this reference. However, what we requested was actually "... reference that reports experimentally realized high refractive index of 3 or above, over broad visible or near-infrared range." We would like to note that it is easy to increase the refractive index with sharp resonances and one can obtain even *almost-stopped light* ("Storage of Light in Atomic Vapor," Phys. Rev. Lett.

86, 783, (2001).) with a gigantic group index. However, the bandwidth reduces narrower and narrower as the resonance is made sharper and sharper. Our approach is different in that we achieved a high refractive index that is nearly constant over a very broad frequency range.

Finally, one of my points in the previous report was misinterpreted. I requested additional explanation on the anisotropy of the scattering, not on the polarization anisotropy, that is also why I asked the author to provide some angular resolved spectra of the sample or at least comment on the anisotropy of the scattering in angle.

We appreciate this comment. We measured the anisotropic scattering of metasurface with respect to the incident angle using FDTD simulations and compared it to that of a thin film made of a uniform effective medium (a uniaxial crystal). The silver nanoparticle structure with shrunken inter-particle distance was used as the metasurface. Gradually changing the angle of incidence, we compared the complex transmission and reflection coefficients calculated from the simulation of the metasurface to the coefficients extracted from an effective anisotropic thin film with a transfer matrix method, in off-resonance regime (at 1000 nm wavelength).

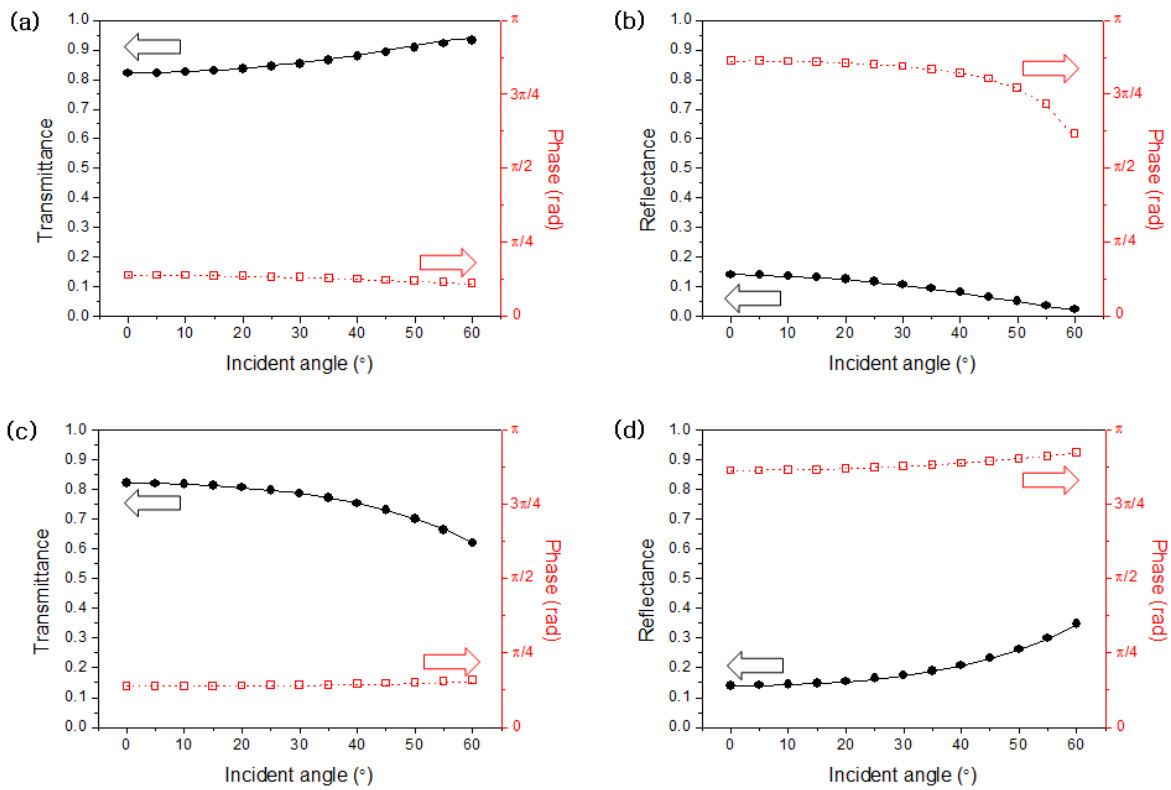


Figure R1 Angle dependence of (a) transmission and (b) reflection for p-polarized incident light of 1000nm wavelength. Intensities are shown with block solid lines (uniform thin film) and black dots

(metasurface) and the phases are plotted with red dotted lines (uniform thin film) and red open squares (metasurface). (c) and (d) are for s-polarized incident light.

In figure R1, one can find that the optical properties of the metasurface are very similar to a uniform effective material for all incident angles considered and for both p- and s-polarizations. (The parameters for the effective material were $\epsilon_x = \epsilon_y = 13.7 + 0.4i$ and $\epsilon_z = 3.8 + 0.7i$.) Since a general illumination with arbitrary polarization and spatial patterns can be decomposed into plane waves with p- and s-polarizations, this result indicates that the metasurface can be modelled with good accuracy as a thin film made of a uniform uniaxial crystal when its linear optical properties are concerned.