Three-Dimensional Infrared Metamaterial with Asymmetric Transmission

Supporting Information

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Structure fabrication

(a) Fabrication of metallic 3D SCR structures

Firstly, dielectric 3D structures were fabricated using an organic-inorganic hybrid material with metal-binding moieties. They were subsequently metallized using electroless plating. The material synthesis, dielectric structure fabrication and silver coating are described in the following paragraphs.

All chemicals were obtained from Sigma-Aldrich, and used without further purification.

Materials Synthesis: The synthesis of the photopolymer used for the fabrication of 3D metamaterial structures on glass substrates has been described previously [1, 2]. It consisted of Methacryloxypropyl Trimethoxysilane (MAPTMS), Zirconium n-Propoxide (ZPO, 70% in propanol,) and 2-(dimethylamino)ethyl methacrylate (DMAEMA). MAPTMS and DMAEMA were used as the organic photopolymerizable monomers, while the latter also served as a metal-binding moiety. ZPO and the alkoxysilane groups of MAPTMS were used to form the inorganic network. Michler's ketone (4,4-bis(diethylamino) benzophenone, BIS) at 1% w/w concentration to the final solution MAPTMS and DMAEMA composite was used as a photoinitiator.

The samples were prepared by drop-casting onto 100 micron-thick silanized glass substrates, and the resultant films were dried in an oven at 50 °C for 10 minutes before photopolymerization.

3D structure fabrication: The DLW experimental setup has been described previously [3]. For the multiphoton polymerization, a Ti:Sapphire femtosecond laser oscillator (800 nm, 75MHz, Femtolasers Fusion) was used. This light source is equipped with integrated dispersive mirrors that pre-compensate the beam delivery and focusing optics to achieve sub-20fs duration pulses inside the sample. The laser beam was focused using a high numerical aperture focusing microscope objective lens (40x, N.A. = 0.95, and 100x, N.A. = 1.4, Zeiss, Plan Apochromat). The photopolymerized structure was generated by moving the sample, using x-y-z piezoelectric and linear stages (Nanocube, PI). The beam was controlled using a mechanical shutter (Uniblitz), while the light intensity was adjusted by a motorized attenuator (Altechna). A CCD camera was mounted behind a dichroic mirror for online monitoring of the polymerization process. The structures were fabricated in a layer-by-layer fashion with the last layer on the surface of the coverslip.

Silver Coating: The metallization process is a modification of that described previously [1, 2], and it comprised three main steps: first, treatment of the structure surface with a metal ion precursor to allow the

binding of the metal species onto the 3D structures. Next a metal reduction step to form the metal nanoparticle seeds on the nanostructures, and finally, a silver bath/plating process to obtain the metal-coated structures.

Thus, 0.08493gr of Silver nitrate ($AgNO_3$) was added in 10 ml of nanopure water (H_2O, 18.2 MΩ cm) for 38-42 hr, in order to create a thin layer of silver ions on the polymer. Secondly, 1.5 gr of sodium-borohydride ($NaBH_4$) was dissolved in 16 ml of H_2O for 20-22 hours in order to reduce the silver ions to nanoparticles. Finally, the solutions mentioned above were mixed at room temperature and were stirred thoroughly until a homogeneous solution was obtained.

For the plating procedure three more solutions were made: 5.47 gr of glucose in 16 ml H_2O, 0.339 gr of $AgNO_3$ in 10 ml H_2O, and 0.37 gr of ammonia in 6 ml H_2O. The solutions above were mixed in a certain sequence; ammonia in silver nitrate solution, and finally the glucose solution. The 3D structured samples were immersed in the resultant solution for 35-60 sec until the color of solution turned to black. Finally, the silver-coated 3D structures were dried in air at room temperature before being measured.

(b) Characterization techniques

The morphology of the 3D metamaterial structures was studied using a Field Emission JEOL JSM 7000F SEM. The samples were sputtered with 5-10 nm gold and the observation was made at 15 kVolts.

Figures S1(a)-(c) illustrate SEM images of the fabricated 3D SCR samples (check Fig. 1 of manuscript for details).

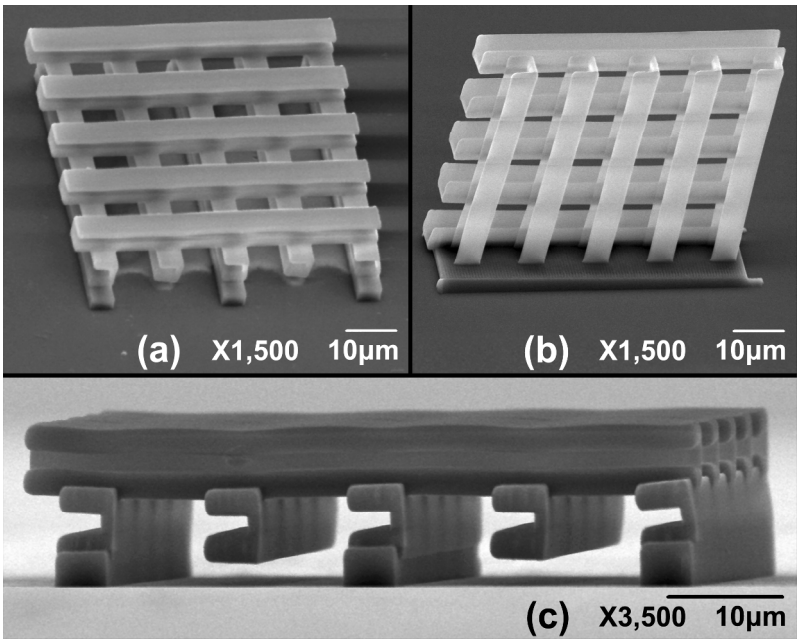

Fig. S1: (a) top view, and (c) side view of SEM images of the 3D SCR metamaterials under consideration. A free-standing version of the 3D SCR structures can be seen in panel (b). All the images were recorded at 15 kVolts, while the magnification scale can be seen below the SEM images.

As it can be observed, the 3D SCR samples are structured accurately, without distortion and no defects or metal remains on the glass substrate.

Polarization transformer response

Taking into account the Stokes Parameters [4] and the approach by Bassiri et al. [5] we calculated the orientation angle (ψ) of the polarization ellipse and the ellipticity angle (χ) (see Fig. S2) of the wave transmitted through the metamaterial structure. This approach is applied to any wave of the form $\mathbf{E} = (E_{\perp}\hat{e}_{\perp} + E_{\parallel}\hat{e}_{\parallel})\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)$ where the unit vectors $\hat{e}_{\perp}, \hat{e}_{\parallel}$ refer to the plane of incidence. (For normal incidence and for an *x*-polarized incident wave propagating along z-direction, as in the case presented in this manuscript, we can consider $\hat{e}_{\perp} = \hat{x}, \hat{e}_{\parallel} = \hat{y}$; thus we have for the transmitted wave $E_{\perp} = T_{xx}$, $E_{\parallel} = T_{yx}$). The four Stokes parameters, which describe completely the state of polarization of the wave [28], are defined by

$$S_0 = E_{\perp} E_{\perp}^{*} + E_{\parallel} E_{\parallel}^{*}, \quad (1)$$

$$S_1 = E_{\perp} E_{\perp}^{*} - E_{\parallel} E_{\parallel}^{*}, \quad (2)$$

$$S_2 = 2\mathrm{Re}\{E_{\perp} E_{\parallel}^{*}\}, \quad (3)$$

$$S_3 = 2\mathrm{Im}\{E_{\perp} E_{\parallel}^{*}\}, \quad (4)$$

where the * denotes the complex conjugate. The power carried by the wave is proportional to S_0, and the orientation angle ψ of the polarization ellipse (see Fig. S2) is given by:

$$\tan(2\psi) = S_2/S_1 \ (0 \le \psi \le 180^{\circ}), \quad (5)$$

and the ellipticity angle χ (see Fig. S2) is given by:

$$\tan\chi = \frac{S_3/S_0}{1+[1-(S_3/S_0)^2]^{1/2}} \ (-45^{\circ} \le \chi \le 45^{\circ}) \ , \quad (6)$$

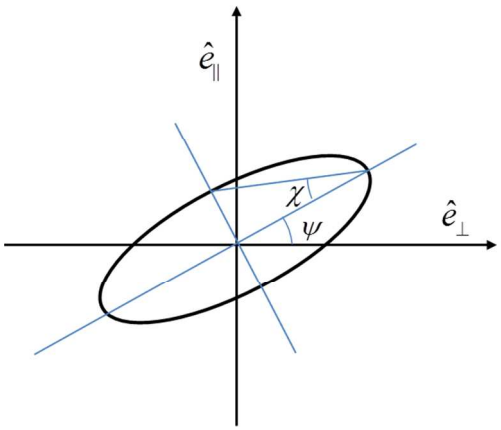

Fig. S2: The polarization ellipse for an elliptically polarized wave with an orientation angle ψ and an ellipticity angle χ.

References

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