Controllable optical negative refraction and phase conjugation in graphite thin films

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Optical metamaterials have demonstrated remarkable physical properties, including cloaking, optical magnetism and negative refraction2–4. The last of these has attracted particular interest, mainly because of its promise for super-resolution imaging5–6. However, the widespread use of negative refraction at optical frequencies is challenged by high losses and strong dispersion effects, which typically limit operation to narrow frequency bands7. Here we use degenerate four-wave mixing to demonstrate controllable negative refraction at a graphite thin film, which acts as a highly efficient phase-conjugating surface. The scheme has very low loss because of the negligible thickness of the nonlinear material and it ensures broadband operation due to the linear band structure of graphene.

Negative refraction has been demonstrated with plasmonic materials8,9 and with discrete nonlinear elements10, but these approaches suffer from high losses and strong dispersion, which restricts operation at optical frequencies to narrow frequency bands5. As an alternative approach, it was proposed that a phase-conjugating surface can act as an analogue of a negative-index material boundary and reverse the phase of the electromagnetic fields. By combining a pair of such closely spaced surfaces it is possible to mimic the silver slab originally proposed in ref. 4 and to achieve diffraction-free super-resolution imaging11.

Phase conjugation has been used in optics for many decades to recover a beam profile that has been distorted by passing through a perturbative medium12. Realization of phase conjugation is based on degenerate four-wave mixing, in which two counter-propagating beams are used to write a holographic grating into a nonlinear crystal, while a third beam is diffracted in a direction exactly opposite to the incident wave. The phase of the diffracted beam is reversed, which is analogous to time-reversed propagation11. Typically, phase conjugation is employed to control the field that is reflected from the surface of a nonlinear medium. Here, we use phase conjugation to control the transmitted, that is, negatively refracted field. To achieve negative refraction, wave propagation in the nonlinear medium has to be negligible, which requires a nonlinear medium of vanishing thickness, such as a graphite thin film (Supplementary Information).

The demonstration of phase conjugation in a two-dimensional system is challenging because the nonlinearity is reduced to a single sheet and because all light fields are of the same frequency, which makes the discrimination of linearly scattered background fields difficult. To circumvent these problems, multi-frequency excitation can be used13. However, when the diffracted beam emerges at a different frequency than the incident signal beam, which destroys any phase relation between input and output. Phase conjugation is not possible with such an approach. In contrast, by using a graphite thin film we are able to achieve negative refraction through phase conjugation, that is, by reversing the phase of the signal beam.

A graphite thin film forms an efficient phase-conjugating surface. Graphene’s third-order nonlinear susceptibility has been shown to be two orders of magnitude larger than that of gold14 and its atomic smoothness greatly suppresses undesired surface scattering. The high nonlinearity of graphene combined with its relatively low absorption makes it a very attractive optical material for two-dimensional phase conjugation.

As shown in Fig. 1a, a negatively refracting lens is generated by illuminating a graphite thin film with two counter-propagating pump beams $E_i \exp (i \mathbf{k}_1 \cdot \mathbf{r})$ and $E_s \exp (i \mathbf{k}_2 \cdot \mathbf{r})$ of angular frequency $\omega$. A signal beam $E_s \exp (i \mathbf{k}_c \cdot \mathbf{r})$ of the same frequency is then refracted at the holographic grating written by the two pump beams. This process can be described by a third-order surface nonlinearity $\chi^{(3)}$ that gives rise to nonlinear surface polarization $^{12} P^{(3)}(\omega) = e_0 \chi^{(3)}(\omega, \omega, -\omega) E_i \exp (i \mathbf{k}_1 \mathbf{r}) E_s \exp (i \mathbf{k}_c \mathbf{r})$.

For counter-propagating pump beams we have $\mathbf{k}_1 + \mathbf{k}_2 = 0$ and hence $P^{(3)} = P_0 \exp (-i \mathbf{k}_c \cdot \mathbf{r}) = P_0 \exp (-i k \sin \theta z)$, where $k \sin \theta_z$ is the projection of wave vector $k_c$ on the graphite surface. The nonlinear surface polarization $P^{(3)}$ gives rise to a secondary field

$$E_i = \left\{ \begin{array}{ll} E^{(1)}_i \exp (-i k \sin \theta z + i k_\perp \cos \theta z) & z > 0 \\ E^{(2)}_i \exp (-i k \sin \theta z - i k_\perp \cos \theta z) & z < 0 \end{array} \right.$$

(1)

with amplitudes $E^{(1)}_i$ that are determined by $P_0$. As $P_0$ is proportional to the conjugate of $E_i$, the secondary field is the phase conjugate of the signal beam. According to equation (1), the graphite thin film yields not only a phase-conjugate reflected wave that propagates against the incident signal beam, but also a negatively refracted beam, which is a direct consequence of the vanishing thickness of the nonlinear medium.

To verify negative refraction as predicted by equation (1) we have performed the experiment illustrated in Fig. 1. The output of a mode-locked Ti:sapphire laser with centre wavelength 800 nm and pulse duration of 200 fs is split into three beams, each of which is focused on the sample from a different angle of incidence. The focal spots of the three beams are overlapped on a graphite thin film sandwiched between two glass hemispheres. A low-numerical-aperture multi-mode fibre picks up the refracted light and sends it to a photodetector. To increase the signal-to-noise ratio and reject spuriously scattered light, the intensity of one of the beams is modulated with an optical chopper and the detected signal is

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demodulated with a lock-in amplifier. The temporal overlap of the laser pulses has been optimized by adjusting the optical path length of the beams and observing the blueshifted multi-photon excited emission from the graphite thin film. 

Samples of graphite thin films were prepared on a fused-silica glass slide by micromechanical cleavage. Suitable flakes were identified with an optical microscope and subsequently characterized by confocal transmission microscopy. The thickness and quality of the graphite films were determined by atomic force microscopy. Graphite flakes consisting of \( \sim 20 \) atomic graphene layers were selected because they provide the best compromise between nonlinear signal generation and absorption. However, we have verified that negative refraction can also be measured on graphite thin films with fewer layers (Supplementary Information). The selected flakes have a lateral size that is significantly larger than the laser spot sizes of \( \sim 10 \mu \text{m} \). A drop of immersion oil is deposited on top of the flake and a second fused-silica glass slide is placed over it. Finally, sub-hemispherical solid immersion lenses (SIL) are bonded to each of the two glass slides and centred over the graphite thin film to ensure that sample rotation does not affect the alignment of the excitation beams (Fig. 1). The sample is then fixed on a rotation stage that is used for tuning the angles of incidence \( \theta_1 \) of the excitation beams. The rotation stage is supported by a translation stage for positioning the flake into the focal region of the excitation beams.

Figure 2 shows our experimental results. The refracted intensity exhibits a resonance at \( \theta_3 - \theta_4 \approx 0^\circ \); that is, the signal beam is refracted in the negative direction as predicted by equation (1). The angular width of the measured curve is defined by the numerical aperture of the external focusing lenses. The signal disappears if one of the excitation beams is delayed in time (curve at the bottom in Fig. 2a). The remaining linear background signal originates from reflections from the outer SIL surfaces. The dependence of the negatively refracted intensity on the time delay of the signal beam is explicitly shown in Fig. 2b. Here, the sample rotation angle is fixed at \( \theta_1 - \theta_4 = 0^\circ \) and the signal beam is delayed by adjusting the path length using a translation stage. The resulting signal pulses exhibit a mean pulse duration of \( \sim 3 \) ps, which is more than an order of magnitude longer than the duration of the initial laser pulses. The increased width is the result of dispersion; that is, the pulses get stretched in time as they travel through the experiment. This has been indeed confirmed by measuring the autocorrelation function of the pulses using the multi-photon excited luminescence as a signal (data not shown). For 10 mW of laser power in each of the excitation beams, the efficiency of negative refraction is found to be 0.1%, which is remarkably high for a nonlinear process. The efficiency can be improved with higher laser powers and tighter focusing, approaching unity for realistic intensity levels. For example, focusing the incident beams to spots of \( \sim 600 \) nm or compressing the pulse durations at the sample to 100 fs will provide sufficiently high intensities for unity conversion,
The scheme provides all-optical control of negative refraction, which can be exploited for many optoelectronic applications. Using graphite thin films as an interface material ensures low-loss operation and virtually unlimited bandwidth.

Received 24 October 2012; accepted 3 April 2013; published online 5 May 2013; corrected online 10 May 2013

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Acknowledgements
This research was financially supported by the US Department of Energy (grant DE-FG02-05ER46207). We thank J. Pendry, B. Deutsch, P. Bharadwaj and A. Jorio for valuable input and fruitful discussions. H.H. acknowledges financial support during the completion of the manuscript from the Center for Nanoscale Materials, which is supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Author contributions
H.H. built the experimental set-up, performed the measurements, analysed the data and contributed to sample fabrication, R.B. fabricated and characterized the samples, L.N. conceived and supervised the project and analysed the data. All authors contributed to discussions and the writing of the manuscript.

Additional information
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Competing financial interests
The authors declare no competing financial interests.
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Nature Physics http://dx.doi.org/10.1038/nphys2618 (2013); published online 5 May 2013; corrected online 10 May 2013.

In the version of this Letter originally published online, the y axis in Fig. 2b was aligned incorrectly. This error has now been corrected in all versions of the Letter.