efficiently in colloidal semiconductor NCs and was first reported experimentally using PbSe NCs in 2004 (ref. 4). In the MEG process, absorption by an NC of a single photon of sufficient energy generates two or more excitons within the NC. Interestingly, colloidally suspended silicon NCs have also been shown to exhibit MEG (ref. 5). However, efficient separation of electrons from holes for multiple excitons within a single NC remains a challenging scientific and technical barrier, with no conclusive reports so far of multiple excitons contributing more than one electron to the photocurrent in a working device. Although the materials system used by Timmerman et al. does not provide an obvious simple route to photocurrent collection, the distinct nature of the resulting excited states may provide another avenue to improving the efficiency with which high-energy photons are used in solar cells. A notable finding in the current work concerns the energy threshold for the process: whereas the energy-conservation threshold for MEG is twice the NC bandgap, $E_{g(Si NC)} \approx 1.36$ eV, the energy threshold for SSQC using 3-nm diameter silicon NCs together with Er^{3+} ions is given by the sum of the NC bandgap and the erbium excitation energy, $E_{Er3+} \approx 0.81$ eV, and is therefore lower.

In semiconductors, photogenerated charge carriers with excess energy above the band edge relax on the subpicosecond timescale through phonon scattering. Thus, the successful generation of multiple excited states (either by MEG or by SSQC) must necessarily compete with the phonon scattering rate. Carrier relaxation dynamics have not been reported for silicon NCs, perhaps owing to measurement complications associated with the indirect bandgap in the electronic structure of silicon. However, in the characterization of cooling dynamics for several other types of NCs such as InP, CdSe and PbSe, the cooling times fall generally in the subpicosecond range. It is noted by Timmerman et al. that cooling may be slower in indirect-bandgap materials such as silicon; nonetheless, it is likely that the SSQC process occurs over very short timescales, perhaps on the order of 100 fs or less. One possible mechanism relates to the extended wavefunction associated with high-energy excitation: the authors propose that the ultrafast energy-transfer process results from an inter-chromophore impact-ionization interaction between the energetic exciton in the silicon NC and a ground-state electron in the neighbouring chromophore. This scenario requires that the chromophores reside very near to one another, and this is indeed the case for the measurements reported thus far (about 50% of the NCs have at least one neighbouring NC within a distance of 1 nm). Interestingly, efficient MEG has been characterized for films consisting of closely spaced and electronically coupled PbSe NCs (ref. 6);

this nanomaterial system may very well benefit from both MEG as well as SSQC, and may indeed eventually lead to a coherent understanding of whether the two processes share common physical origins.

The evident demand for inexpensive carbon-free energy continues to drive research and development on novel approaches to generate electricity and fuels from sunlight. As silicon accounts for more than 90% of global photovoltaic-cell production, this report of space-separated quantum cutting in silicon NC systems illuminates an important possible route towards the goal of inexpensive and highly efficient solar-energy conversion. As remains the case with the MEG process, significant questions must be answered regarding the mechanism, dynamics and absolute efficiency of SSQC. The ultimate impact of SSQC to solar energy conversion depends on its ability to survive the tests of careful scrutiny, the absolute efficiency with which it occurs and our ability to efficiently exploit this nanoscale process in macroscopic devices.

References

1. Timmerman, D., Izeddin, I., Stallinga, P., Yassievich, I. N. & Gregorkiewicz, T. Nature Photon. **2,** 105–109 (2008).
2. Kenyon, A. J., Trwoga, P. F., Federighi, M. & Pitt, C. W. J. Phys.: Condens. Matter **6,** L319–L324 (1994).
3. Fujii, M., Yoshida, M., Kanzawa, Y., Hayashi, S. & Yamamoto, K. Appl. Phys. Lett. **71,** 1198–1200 (1997).
4. Schaller, R. D. & Klimov, V. I. Phys. Rev. Lett. **92,** 186601 (2004).
5. Beard, M. C. et al. Nano Lett. **7,** 2506–2512 (2007).
6. Luther, J. M. et al. Nano Lett. **7,** 1779–1784 (2007).

LIGHT AND MATTER INTERACTIONS
Going with the grain

Non-reciprocal optical phenomena — effects that depend on the direction of light propagation — are rare. Researchers have now observed non-reciprocal material modification when moving a beam of ultrashort light pulses through a lithium niobate crystal.

Chris B. Schaffer

is in the Department of Biomedical Engineering, Cornell University, Ithaca, New York 14853, USA.

e-mail: cs385@cornell.edu

It is well known that a tightly focused femtosecond laser pulse can heat up a microscopic volume inside a transparent sample, such as glass. For more than ten years, researchers have been studying this phenomenon and using it to micromachine miniature devices and fabricate three-dimensional waveguides. However, until the work by Weijia Yang and colleagues reported on page 99 of this issue[1], little research has focused on whether the direction of the light beam's propagation can influence the effects induced in the material.

Now, Yang and colleagues have shown that material modifications induced by femtosecond laser pulses can be distinctly different when a laser beam propagates in opposite directions. Their tests were performed with a $LiNbO_3$ crystal — an anisotropic crystal widely used in nonlinear photonics applications[1].

Phenomena that are non-reciprocal are uncommon in optics. In Faraday rotation,

the direction in which the polarization of linearly polarized light rotates depends on whether the light propagates parallel or antiparallel to an applied magnetic field. This effect is often used to produce optical isolators that act as one-way valves for light. No previous studies, however, have demonstrated non-reciprocal optically induced modification of material properties.

In recent years, femtosecond laser irradiation has provided a new means of locally altering the optical properties of transparent materials. When a femtosecond laser pulse is tightly focused

in the bulk of a transparent material, the intensity in the focal region can become high enough to induce nonlinear optical absorption[2]. Both multiphoton ionization (the simultaneous absorption of multiple photons to ionize an electron) and avalanche ionization (the impact ionization of an electron by another electron that has absorbed energy from the laser) lead to the production of a hot electron–ion plasma in the material[3].

Nonlinear absorption deposits laser energy in the material, but only in the micrometre-sized focal region where the laser intensity is high. When enough energy is deposited in the focal volume, permanent material alterations can be produced, ranging from the formation of small refractive-index changes[4] to voids[5]. This femtosecond-laser-induced material modification has been demonstrated in several substances including glass[4,5], crystalline materials[6] and transparent polymers[7], and has been used to fabricate three-dimensional optical devices[8] and microfluidic channels[7,9], for example.

Although most femtosecond micromachining has been performed using a series of laser pulses that act more or less independently to alter the material, it is also possible to use cumulative effects. When the repetition rate of the laser is sufficiently high, so that the time between laser pulses is shorter than the characteristic time for energy to be transported out of the focal volume, there can be an accumulation of heat in the focal region[10–12]. This heating will melt the material around the focal region and, when the laser irradiation is removed, this melted region will rapidly cool down, leading to changes in the material properties.

The volume of the affected region increases with the energy deposited by each pulse as well as with the total number of pulses that irradiate the area[11,12]. In effect, the laser serves as a small source of heat that can be localized within the bulk of a transparent material. If the laser focus is translated along a line through a glass sample while continuously irradiating, a cylindrical region with an altered refractive-index profile is produced, creating a high-quality optical waveguide[8].

Now imagine that the heat flow out of the focal volume is anisotropic, in other words different along different directions. If the focus of the laser beam is translated along a direction where heat flow is more efficient, the temperature in the focal volume will increase owing to both the absorption of new laser energy as well as the flow of heat from energy that is absorbed in the adjacent volume. The result is a higher temperature than would be achieved
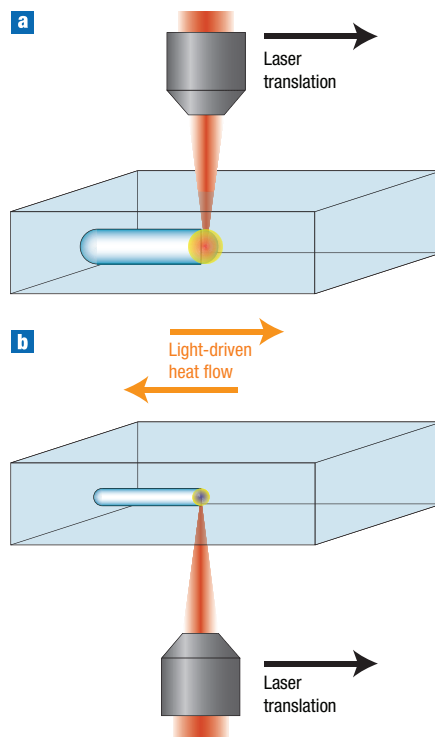
Figure 1 Directional light–matter interactions. **a**, Light-driven thermal currents lead to greater material heating and therefore more pronounced material modification when the laser focus is translated along the direction of the heat flow. **b**, When the propagation direction of the laser is reversed, the direction of the light-driven thermal current also reverses, so the heat flows in the opposite direction to the laser translation, leading to less sample heating and less pronounced material modification.

with only isotropic thermal diffusion, and therefore more pronounced material modifications. Conversely, translating the laser focus along a direction where the heat flow is less efficient will lead to less heating of the material in the focal region.

The experiments of Yang et al. show that the heating-induced material modifications in $LiNbO_3$ are different if the laser focus is translated along the $+y$ and $-y$ axes of the crystal. Why is heat flow along one crystal axis different for opposite directions? The answer is that when the electron–ion plasma produced by the femtosecond laser pulse is exposed to the strong electric field of the laser pulse, the electric field of the laser can influence the net motion of the electrons by pondermotive (net motion down the laser intensity gradients) and photon-drag forces.

The speed of the electron motion depends on the direction of the laser propagation, the polarization direction of the laser and, importantly, on two sixth

rank tensors that characterize the material properties. Owing to differences in the magnitude of off-axis elements in these tensors, the net electron motion along the $+y$ and $-y$ directions of a $LiNbO_3$ crystal differ.

This difference leads to a net thermal current along the $-y$ axis when the laser is incident along the $+z$ direction and polarized along the y axis. This heat flow is in addition to the transport of heat by thermal diffusion and it leads to more heating of the sample when the laser focus is translated in the $-y$ direction — along the direction of net heat flow — compared with along the $+y$ direction. This greater heating explains the more pronounced material changes that are observed by Yang et al. for translation along the $-y$ direction[1]. In contrast, no difference is observed in the induced material change when the laser focus is translated along the $+x$ or $-x$ axes[1] where heat transport is not directional.

Interestingly, if the incident direction of the femtosecond laser changes from the $+z$ to the $-z$ crystal axis, the direction of light-driven heat flow changes from $-y$ to $+y$, leading to a reversal of the laser translation direction that causes greater sample heating and therefore more pronounced material alterations, as shown in Fig. 1 (see ref. 1). Thus Yang, et al. have shown that non-reciprocal material modification results from a change in the direction of light-induced heat flow when the laser propagation direction is reversed[1].

In conclusion, non-reciprocal phenomena are rare in nature and one that leaves a permanent mark is even more unusual. Although it is not immediately clear how non-reciprocal photosensitivity in $LiNbO_3$ or possibly other anisotropic materials may benefit materials processing applications, it is apparent that this effect will need to be taken into account in the future.

References

1. Yang, W., Kazansky, P. G. & Svirko, Y. P. Nature Photon. **2**, 99–104 (2008).
2. Schaffer, C. B., Brodeur, A. & Mazur, E. Meas. Sci. Technol. **12**, 1784–1794 (2001).
3. Stuart, B. C. et al. Phys. Rev. B **53**, 1749–1761 (1996).
4. Schaffer, C. B., Jamison, A. O. & Mazur, E. Appl. Phys. Lett. **84**, 1441–1443 (2004).
5. Glezer, E. N. et al. Opt. Lett. **21**, 2023–2025 (1996).
6. Thomson, R. R., Campbell, S., Blewett, I. J., Kar, A. K. & Reid, D. T. Appl. Phys. Lett. **88**, 111109 (2006).
7. Kim, T. N., Campbell, K., Groisman, A., Kleinfeld, D. & Schaffer, C. B. Appl. Phys. Lett. **86**, 201106 (2005).
8. Kowalevicz, A. M., Sharma, V., Ippen, E. P., Fujimoto, J. G. & Minoshima, K. Opt. Lett. **30**, 1060–1062 (2005).
9. Ke, K., Hasselbrink, E. F. & Hunt, A. J. Anal. Chem. **77**, 5083–5088 (2005).
10. Schaffer, C. B., Brodeur, A., Garcia, J. F. & Mazur, E. Opt. Lett. **26**, 93–95 (2001).
11. Schaffer, C. B., Garcia, J. F. & Mazur, E. Appl. Phys. A **76**, 351–354 (2003).
12. Eaton, S. M., Zhang, H. B. & Herman, P. R. Opt. Express **13**, 4708–4716 (2005).