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Giant refractive-index modulation by two-photon reduction of fluorescent graphene oxides for multimode optical recording

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Received
24 April 2013Accepted
29 August 2013Published
2 October 2013

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SUBJECT AREAS:
OPTICAL DATA STORAGE
OPTICAL PROPERTIES AND DEVICES
NONLINEAR OPTICS
OPTICAL MANIPULATION AND TWEEZERS

Graphene oxides (GOs) have emerged as precursors offering the potential of a cost-effective and large-scale production of graphene-based materials. Despite that their intrinsic fluorescence property has already brought interest of researchers for optical applications, to date, refractive-index modulation as one of the fundamental aspects of optical properties of GOs has received less attention. Here we reported on a giant refractive-index modulation on the order of 10^{-2} to 10^{-1} , accompanied by a fluorescence intensity change, through the two-photon reduction of GOs. These features enabled a mechanism for multimode optical recording with the fluorescence contrast and the hologram-encoded refractive-index modulation in GO-dispersed polymers for security-enhanced high-capacity information technologies. Our results show that GO-polymer composites may provide a new material platform enabling flexible micro-/nano-photonic information devices.

wing to its intriguing electronic and optical properties, graphene¹ has been heralded as the next generation material for electronic and photonic devices^{2–4} since its emergence. Reduced graphene oxide (GO) resembles graphene yielding similar physical properties, but with some residual oxygen and structural defects, which offers a cost-effective approach for the large-scale production of graphene-based materials^{5–7} as well as graphene-polymer composites^{8,9}. Its integration with nanofabrication techniques including near-field scanning tips^{10,11} and electron beam lithography^{12,13} is essential to manipulate the nanoscale electronic and optical properties, which has accelerated the development of graphene-based micro-/nano- devices. In this regard, focusing a high-intensity laser beam has become an indispensable tool for maskless and far-field micro-manipulating of the reduced GOs within a sub-wavelength scale^{14,15}. The essence of this technique is that a localized photoreduction process within the focal region can be introduced and the degree of the reduction thus electronic properties can be well controlled by light, which sets a new landmark for flexible micro-supercapacitors¹⁵.

In contrast to graphene, the observation of a broadband fluorescence emission is the most notable optical property of GOs and reduced GOs, which is somewhat an unexpected consequence of their heterogeneous atomic and electronic structures¹⁶. The strong fluorescence emission from GOs has led to intriguing applications in bioimaging¹⁷. In addition, the two-photon reduction by a fs pulsed laser beam enabled reduced GO nanoparticles as nonbleaching probes for the photothermal cancer therapy¹⁸. The intrinsic structure change from GOs to reduced GOs indicates a possible refractive-index modulation. Nevertheless, refractive-index modulation as one of the most important optical properties of GOs has been far less explored. In fact, a large refractive-index modulation within a sub-wavelength scale is crucial, which provides a core foundation for electro-optic effects and underpins nearly entire light-enabled principles. As such, focusing a femtosecond (fs) pulsed laser beam to introduce a localized refractive-index change has enabled tremendous progresses on developing nanophotonic devices such as nanofabrication and ultra-high density optical data storage^{19,20}.

In this communication, we report on a giant refractive-index modulation on the order of 10^{-2} to 10^{-1} by the controlled photoreduction of fluorescent GOs through focusing a fs pulsed laser beam. The giant refractive-index modulation in conjunction with the simultaneous fluorescence change offers a mechanism for multimode optical recording with both the fluorescence contrast and the hologram-encoded refractive-index modulation in the



GO-polymer composites, enabling an enhanced information security and capacity. Most importantly, the GO-polymers build up an excellent material platform for refractive-index-based nanophotonic applications with flexibilities, reliabilities, scalabilities and low costs.

Results

GO water suspension was prepared following a well-established recipe (Methods)²¹. Poly(vinyl alcohol) (PVA) water solution with a concentration of 20 wt% was prepared. The GO water suspension was added into the PVA solution to yield an ultimate concentration of 1 wt% in the total mixture. Then the mixture was immediately subjected to the sonication at room temperature for 3 h to obtain uniform dispersions. The mixture suspension (Fig. 1a) was spun coated on a cover glass at 1000 rpm and left dry at 60°C. Fig. 1 schematically illustrates the procedure of the focused fs laser beam induced photoreduction in the GO-polymer. The degree of the photoreduction of GO-polymer to reduced GO-polymer can be controlled by the exposing laser intensity, therefore leading to a giant refractive-index modulation and a decrease in fluorescence intensities (Fig. 1b). By laterally translating the sample with respect to the focal spot, image patterns can be recorded into the GO-polymer by either the fluorescence variation or the hologram-encoded refractive-index modulation (Fig. 1c).

Owing to its highly spatial confinement, a fs laser beam at the wavelength of 800 nm was employed for the two-photon reduction as described in our previous work (Methods)¹⁸. The two-photon reduction of GO-polymers into reduced GO-polymers was evident by the micro-Raman spectroscopy. Raman spectra of the GO-polymer sample display two broad peaks at 1354 and 1599 cm^{-1} , corresponding to the D and G bands, respectively (Fig. 2a). The G band is associated with the vibration of sp² bonded carbon atoms, while the D band is generally related to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite. The peaks of both D and G bands of the reduced GO-polymer became distinct and the bandwidths are slightly narrower compared with those of the GO-polymer. The relative intensities between the D and G bands (I_D/I_G) increased from 1.04 to 1.12 in the irradiated region, which can be explained as a decrease in the size of reduced GO domains²².

The as-prepared GO-polymer with a thickness of 25 μm is highly fluorescent. The fluorescence emission arises from the recombination of electron-hole pairs in localized electronic states originating from heterogeneous atomic and electronic structures. Under the excitation by a fs beam at the wavelength of 800 nm, a broad two-photon-excited fluorescence from 550 nm to 750 nm (inset of Fig. 2b) was observed in GO-polymers which is consistent with GO nanoparticles in the previous report¹⁸. Fig. 2b shows that the two-photon fluorescence intensity of the reduced GO-polymer generated at a variety of powers of the fs laser beam normalized to

that of the GO-polymer. It can be seen clearly that the two-photon reduction causes a significant decrease in fluorescence intensities of the reduced GO-polymer and the fluorescence change can be tuned by the strength of the photoreduction through judicious control of the exposure intensity. The dropping in fluorescence intensities in the reduced GO-polymer may be attributed to the loss of its oxygen-containing functional groups²³ during the photoreduction.

The fluorescence decrease by the two-photon reduction opens the potentials of recording and retrieving information in the volume of the GO-polymer. By laterally translating the sample across the focal plane, a grating of reduced GO-polymers with a period of 4.5 μm and a duty cycle of 1/2 was patterned at the power of 5 mW. A two-photon fluorescence image of the recorded grating can be clearly revealed (upper panel of the inset of Fig. 2c). Moreover, the grating can also be retrieved through its diffraction image by using a collimated beam at the wavelength of 632 nm (bottom panel of the inset of Fig. 2c). The normalized diffraction efficiency defined as the intensity ratio between the first order and the zeroth order diffraction is plotted as a function of the fs laser power in Fig. 2c. The large diffraction efficiency obtained implies a large refractive-index modulation by the reduced GOs.

To quantify the refractive-index modulation by the reduced GOs, a GO thin film of a thickness of 2 μm without PVA polymers was prepared. Gratings of reduced GOs with the same period and the same duty cycle were recorded at a variety of fs laser powers. The laser-heating induced height decrease generally accompanies the photoreduction¹⁴. After absorbing the successive fs pulses with a power of 15 mW, the GOs rise the temperature to $\sim 320^\circ C$ (Fig. S1). The heating at this temperature can introduce a mass loss of oxygen-containing groups²⁴, which is clearly evident in the irradiated region in atomic force microscope (AFM) images (Fig. S2). From the measured diffraction efficiencies, the contribution of the laser-induced height change and the refractive-index change by reduced GOs to the overall phase modulation (Methods) (Fig. S3) can be extracted by treating the grating of reduced GOs as a pure phase type, provided that the transmission difference between GOs and reduced GOs is negligible at the detection wavelength of 632 nm²⁵.

The overall phase modulation ϕ can be expressed as a sum of the laser-induced height change and the refractive-index change by the reduced GOs (inset of Fig. 3),

$$\phi = [\Delta n \cdot (d - h) - h] \cdot 2\pi / \lambda \quad (1)$$

where d is the thickness of the GO thin film, h is the laser-induced height change and Δn is the refractive-index modulation by the two-photon reduction of GOs to reduced GOs. Fig. 3 shows the extracted refractive-index modulation by reduced GOs as a function of the laser power in terms of Eq. (1). It reveals clearly that the two-photon reduction of GOs exhibits a giant refractive-index modulation on the order of 10^{-2} to 10^{-1} , which is two orders of magnitude larger than

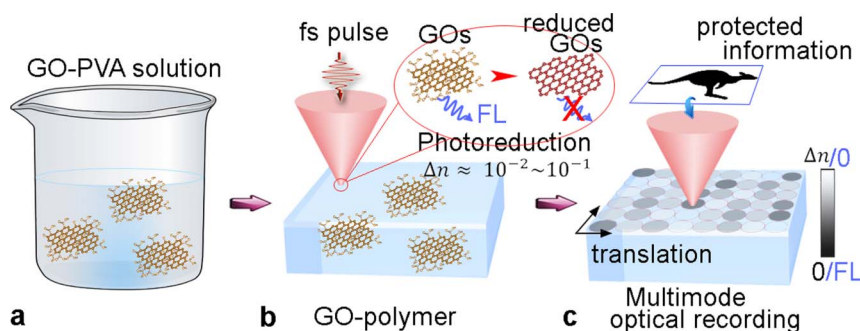


Figure 1 | (a) Mixing GOs with PVA solutions for the preparation of the GO-polymer sample. (b) Illustration of the two-photon reduction induced giant refractive-index modulation and the simultaneous fluorescence (FL) intensity decrease by a fs beam. (c) The giant refractive-index change and FL signals enabled multimode optical recording by laterally translating the sample across the focal plane and controlling the strength of the two-photon reduction.

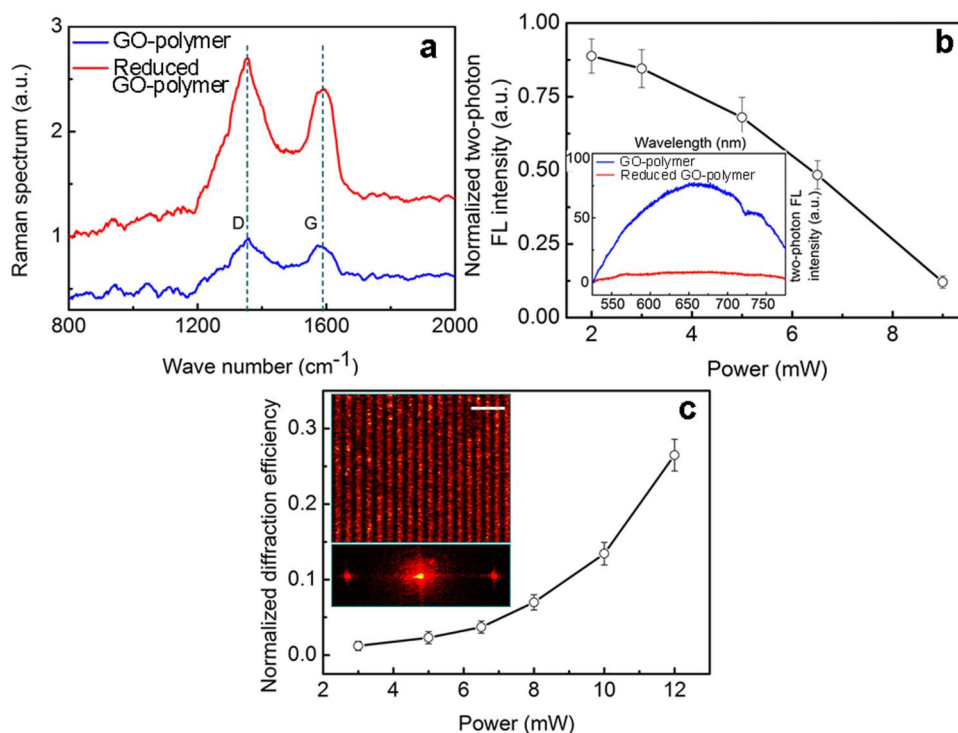


Figure 2 | (a) Raman spectra of the GO-polymer and the reduced GO-polymer. The dashed lines indicate the D and G bands, respectively. (b) The two-photon FL intensity of the reduced GO-polymer generated by a variety of fs laser powers normalized to that of the GO-polymer. The inset shows the two-photon FL spectra of the GO-polymer and the reduced GO-polymer, respectively. (c) The normalized diffraction efficiency in the GO-polymer as a function of the fs laser power. The insets show the two-photon FL image (upper panel) and the diffraction image (bottom panel) of a grating of the reduced GO-polymer. The scale bar is $30 \mu\text{m}$.

the fs laser-induced refractive-index modulation in many other optical media such as lithium niobate²⁶. Most importantly, the sub-wavelength-scale refractive-index change can be also controlled through modulating the strength of photoreduction by the intensity of light.

This unique feature of the sub-wavelength-scale giant refractive-index modulation together with the fluorescence property of the reduced GO-polymer offers a mechanism for multimode optical recording. The two-photon reduction of the GO-polymer exhibits a highly spatial confinement which is highly desired in the

volumetric bit-by-bit recording. The multi-layer information of a kangaroo and a koala can be patterned in the volume of the GO-polymer with a layer separation of $20 \mu\text{m}$ at the power of 5 mW and an exposure time of 10 ms for individual bits. Figs. 4a and b show that the patterned multi-layer information can be distinctively retrieved back through a two-photon fluorescence imaging process. Based on the lateral bit size of $1.5 \mu\text{m}$ and the layer separation of $20 \mu\text{m}$ by a low numerical aperture (NA) objective (NA = 0.4), the

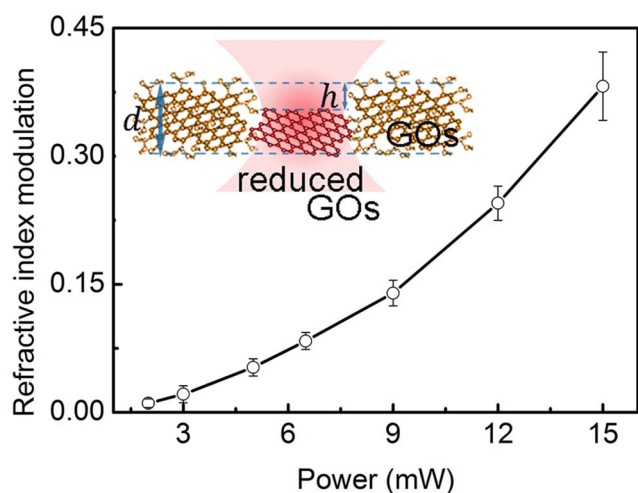


Figure 3 | The refractive-index modulation by reduced GOs as a function of the fs laser power. The inset shows the schematic illustration of the overall phase modulation originating from both the laser-induced height change and the refractive-index modulation from GOs to reduced GOs.

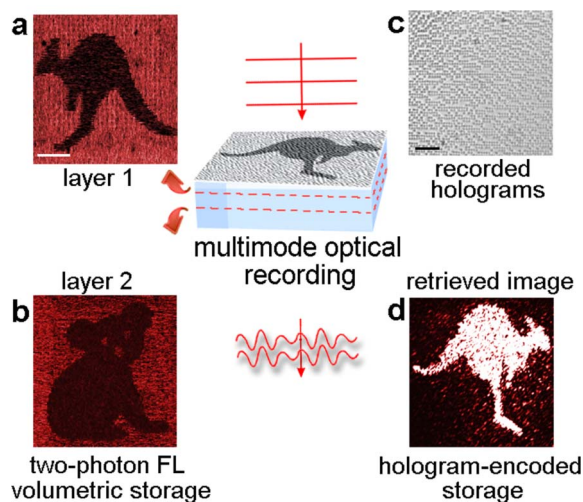


Figure 4 | (a) and (b) Two-photon FL images of the patterns recorded in the volume of the GO-polymers with a layer separation of $20 \mu\text{m}$. The scale bar is $10 \mu\text{m}$. (c) The wide-field transmission image of one section of the holograms produced by the photoreduction-induced refractive-index modulation. The scale bar is $30 \mu\text{m}$. (d) The retrieved image of the protected patterns in the diffraction mode.



demonstrated equivalent density reaches $0.2 \text{ Tbits} \cdot \text{cm}^{-3}$. It should be noted that further increasing the capacity is possible by increasing the NA of the objective.

In conjunction with the fluorescence intensity change, the dependence of the giant refractive-index modulation Δn on the fs laser intensity enables encoding information in the bit-by-bit digital holograms in the same medium for an enhanced information security, where the small refractive-index change ($\sim 10^{-3}$) in photorefractive materials by a fs laser beam^{26,27} may limit its physical realization owing to unreliable and insufficient diffraction efficiencies. To demonstrate its feasibility, the image of a kangaroo was encoded in the computer generated holograms consisting of arrays of discrete phase modulation levels by using a Fourier iterative algorithm²⁸. Then, the hologram was recorded by laterally translating the GO-polymer with respect to the focal spot with variant intensities at individual positions to generate corresponding phase modulations. The protected information in the recorded hologram cannot be retrieved in the normal microscope images (Fig. 4c). While the information can be clearly viewed in the diffracted image with sufficient diffraction efficiencies by using a low-power HeNe laser beam (Fig. 4d). The demonstrated multimode optical recording opens up the potential of applying GO-polymers to optical security tags²⁹ and ultra-secure encryptions²⁰.

Discussion

In conclusion, we have investigated the two-photon reduction of fluorescent GOs by a fs pulsed laser beam. A giant refractive-index modulation on the order of 10^{-2} to 10^{-1} can be realized by controlling the strength of the photoreduction of GOs. The large phase modulation in conjunction with the fluorescence property of GO-polymers offers multimode optical recording for high-capacity information technologies with an enhanced security and reliability. In addition, the photoreduction in the GO-polymer with a capability of the sub-wavelength-scale giant refractive-index modulation together with the ultra-high conductivity control^{14,15} provides a unique platform for developing integrate nanophotonic circuits and electro-optic devices.

Methods

GO synthesis. GOs were prepared with a well-established recipe by the chemical oxidation of natural graphite followed by the exfoliation using sonication for 2 h in water²¹. Unexfoliated particles were removed by centrifugation at 12000 rpm for 20 min. The brown supernatant contained $\sim 3 \text{ mg/ml}$ of GOs was obtained.

Two-photon reduction system. A fs pulsed laser beam at the wavelength of 800 nm (a repetition rate of 82 MHz and a pulse width of 100 fs) was employed for the photoreduction. The laser beam was focused by an objective lens with the numerical aperture of 0.4 down to a lateral size of $1.5 \mu\text{m}$ in the focal area. The laser intensity was controlled by rotating the angle between the direction of the light polarization and the polarizer. The patterned photoreduction was realized by laterally translating the sample across the focal plane.

Characterization of the phase modulation strength. The diffraction intensities of a collimated He-Ne laser beam were measured for GO thin films. The ratio of the first order to the zeroth order diffraction intensities was employed to characterize the phase modulation strength following³⁰

$$R = \frac{F * 4/\pi^2 * \text{SIN}(\Delta\phi/2)^2}{(1-F) + F * \cos(\Delta\phi/2)^2} \quad (2)$$

where F is the filling factor determined by the ratio of the grating area to the beam size and $\Delta\phi$ is the phase modulation strength.

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Acknowledgements

This work was partly supported under the Australian Research Council Discovery Project scheme (DP110101422). Min Gu acknowledges the support from the Australian Research Council Laureate Fellowship program (FL100100099). Xiangping Li acknowledges the Australian Postdoctoral Fellowship support from the Discovery Project (DP110101422).

Author contributions

M.G. and X.L. proposed the idea and the strategy for experimental design and data analysis and completed the writing of the paper. X.L. completed the experiment characterization and multimode recording. X.L. and Q.Z. carried out the AFM characterization. X.C. performed the chemical synthesis of GOs.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Li, X., Zhang, Q., Chen, X. & Gu, M. Giant refractive-index modulation by two-photon reduction of fluorescent graphene oxides for multimode optical recording. *Sci. Rep.* **3**, 2819; DOI:10.1038/srep02819 (2013).



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