

Ultrafast Dynamics and Nonlinear Optical Responses from sp^2 - and sp^3 -Hybridized Domains in Graphene Oxide

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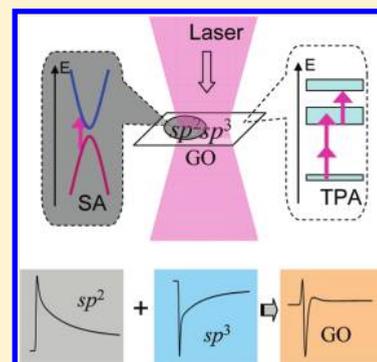
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S Supporting Information

ABSTRACT: The ultrafast relaxation dynamics and nonlinear optical response in single- and few-layered graphene oxide (GO) were studied by ultrafast optical differential transmission spectroscopy and Z-scan technique using various pump intensities. It was found that charge carriers with subpicosecond-to-picosecond dynamics from sp^2 -hybridized domains dominate the ultrafast response at low pump intensities, like graphene. Surprisingly, the influence of two-photon absorption from sp^3 -hybridized domains on the transient absorption signal becomes increasingly strong with pump intensities. On the basis of heterogeneous ultrafast dynamics of GO with saturable absorption in sp^2 domains and two-photon absorption in sp^3 domains, the nonlinear optical response can be tailored by manipulation of the degree and location of oxidation on GO sheets; this unravels the important role of sp^3 domains in graphene optics and will facilitate the potential applications of GO in optoelectronics.

SECTION: Kinetics, Spectroscopy



Graphene has attracted extensive interest of physicists because of its unique electronic structure with linear dispersion of Dirac electrons.¹ The ultrafast carrier dynamics, combined with large absorption and Pauli blocking, make graphene an ideal ultrabroadband and fast saturable absorber in the application of ultrafast laser.^{2–4} The photoinduced bleaching dynamics of charge carriers in graphene have been executed using pump–probe technique and fast decay times from tens to hundreds of femtosecond were assigned to carrier–carrier scattering and carrier–phonon scattering.^{5–10} Recently, tailoring band gap and electrical and optical properties of graphene has become a subject of intensive research in the context of nanoscale optoelectronics.^{11,12} Hence, researchers are increasingly drawn to chemically derived graphene oxide (GO) because of its heterogeneous chemical and electronic structures, along with the fact that it can be processed in solution.^{13,14}

GO is synthesized by the oxidation of graphene, and its unique atomic and electronic structure has been elucidated so that small sp^2 carbon clusters are isolated by the sp^3 matrix.^{13–16} The presence of pristine graphitic nanoislands, that is, sp^2 -hybridized domains, makes GO hold some characteristics of ultrafast carrier dynamics in the graphene.¹⁴ The tunable fluorescence in GO has been observed as a result of the heterogeneous atomic and electronic structure.^{17,18} Herewith, it is expected that there are a heterogeneous optical transition and nonlinear dynamic in GO. However, very little is known about the nonlinear properties and the carrier dynamics of GO, whereas they are key issues for understanding and developing their optoelectronic properties.¹⁹

Furthermore, in contrast with well-established electronic structure of graphene as a zero-gap semiconductor with sp^2 -hybridized carbon atoms,¹ it is still a challenge to determine the fundamental properties of GO such as energy band gap, optical properties, and electronic structure due to its nonstoichiometric chemical composition.^{13,14}

Here we report on the first observation of a heterogeneous nonlinear optical response contribution to the transient differential transmission in GO. We identify this effect through probing GO with different oxidation degree and location. With increasing pump intensities, the transient optical response exhibits a crossover from bleaching to enhanced absorption as two-photon absorption (TPA) of sp^3 domains becomes more prominent. Because of the nonstoichiometric nature of GO, manipulation of the size, location, and relative fraction of the sp^2 domains of GO by chemical methods provides opportunities for tailoring its nonlinear optical properties.

In our experimental study, we made use of three kinds of GO with different oxidation: (i) single-layered graphene oxide (SGO) prepared by chemical exfoliation with enough oxidation; (ii) few-layered graphene oxide (FGO1) with three to four layers prepared by chemical exfoliation with less oxidation;²⁰ and (iii) few-layered graphene oxide (FGO2) with three to five layers prepared by an arc-discharge method.²¹ In SGO, a large fraction

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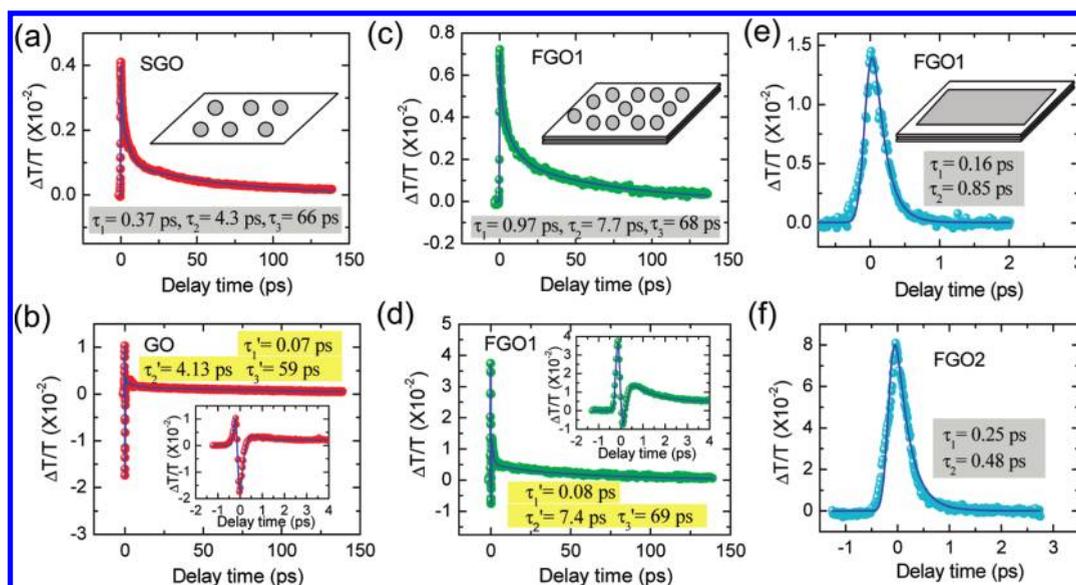


Figure 1. Transient differential transmission spectra of SGO, FGO1, and FGO2 in DMF solutions as a function of pump–probe delay at pump intensities of 5.2 GW/cm² (a,c,e) and 411 GW/cm² (b,d,f). The insets of parts a, c, and e are the schematic of structural morphology of SGO, FGO1, and FGO2, where the gray region and white region represent the sp² domains and sp³ domains, respectively. In the insets of b and d, the differential transmission curves are magnified around zero delays. The solid lines are fits based on the model described in the text, which include both sp² and sp³ domain contributions to the optical response.

(60%) is sp³-hybridized and covalently bonded with oxygen mostly on the basal plane, whereas a smaller amount is present primarily at the sheet edges.²² X-ray diffraction (XRD) and thermogravimetry analysis (TGA) show that there are more sp² clusters in FGO1 than in SGO.²⁰ Although FGO2 has a similar layer distribution to FGO1, most of the disordered oxidation domains exist at the sheet edges, and much larger fraction of sp² domains is located on the basal plane.²¹ The insets of Figure 1a–c show the schematic structures of SGO, FGO1, and FGO2, respectively. All samples were well-dispersed in *N,N*-dimethylmethanamide (DMF).

Figure 1a,c,e shows the measured transient differential transmission spectra for GO, FGO1, and FGO2 at low pump intensity of 5.2 GW/cm². For three kinds of GO, the pump-induced change of transmission is dominated by photobleaching (PB) of the absorption, resulting in a positive differential transmission $\Delta T/T_0 = (T - T_0)/T_0$, T and T_0 are the sample transmissions with and without excitation, respectively. This behavior arises from Pauli blocking of the strong interband optical transitions in the sp² domains, which has been observed in all ultrafast pump–probe measurements of graphene to date.^{5–11} The data were fitted using an exponentially decaying function, $\Delta T/T_0 = \sum_i A_i \exp(-t/\tau_i)$, convoluted with the cross correlation of the pump and probe pulses. In general, the carrier dynamics of graphene meet a biexponential decay with time constants of a few hundreds of femtoseconds and a few picoseconds. The relaxation of a few hundreds of femtoseconds is attributed to thermalization via carrier–carrier scattering and carrier–phonon scattering. So far, it has been argued that the optical excitation leaves the electronic structure out of equilibrium for several picoseconds. Optical phonon cooling,²³ electron–hole recombination,¹⁰ and photoinduced structure instabilities²⁴ may contribute to the decay of several picoseconds. For SGO and FGO1 with graphitic nanoislands, however, a triexponential decay must be used in fitting of relaxation data. The long time decay with a characteristic time

>60 ps was observed in SGO and FGO1, which is fundamentally different from pristine graphene.^{5–10,23,24} We consider that the emergence of long time decay is associated with confined sp² clusters. From Raman and imaging analysis, it has been suggested that GO consists of ~ 3 nm sp² clusters, covering between 1 and 6 nm, and isolated within sp³ carbon matrix.^{13,15,22} The presence of localized finite-sized molecular sp² clusters within a sp³ matrix can lead to confinement of π -electrons in SGO and FGO1. A broad fluorescence in GO indicates the presence of radiative recombination of electron–hole pairs and local energy gap in such sp² clusters. On the basis of Gaussian and density functional theory calculation, the sp² cluster with a diameter of ~ 3 nm has an energy gap of ~ 0.5 eV,¹⁸ as shown in Figure 2. The band gap opening can slow the carrier recombination after excitation.

In GO, the introduction of oxygen-containing functional groups with C–O bonds results in a transformation of carbon atom from sp² to sp³ hybridization. A large energy gap ranging from 2.7 to 3.1 eV for sp³-bonded carbons has been reported in amorphous carbon.²⁵ There is a large energy gap (carrier transport gap) between the σ states of its sp³-bonded carbons in GO (Figure 2),¹⁴ similar to that of amorphous carbon, because the structure of the sp³ domains in GO is predominantly amorphous as a result of distortions from sp³ C–O bonds.²⁶ Therefore, the optical transmittance will increase with the degree of oxidation from visible to near-infrared ranges, which is consistent with line transmittance of 11, 46, and 82% for FGO2, FGO1, and SGO at 1.55 eV. At low pump intensity, the optical transition at 1.55 eV in the sp³ domains is forbidden, and the optical absorption decreases as state filling of the interband transitions in the sp² domains dominates the transient response. Because most sp²-hybridized domains inside FGO2 remain during the oxidization process and oxygen-containing functional groups mainly locate at the edges, the structure of interlayer spacing inside FGO2 is similar to that of normal graphite. Therefore, FGO2 has a fast decay time like the pristine graphene. The relaxation of FGO2

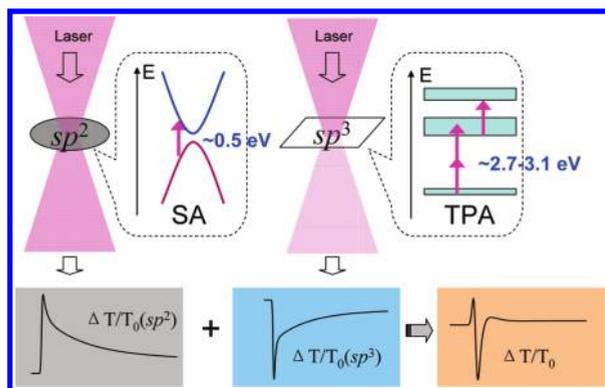


Figure 2. Schematic drawing of a transient absorption in sp^2 and sp^3 domains: SA, saturable absorption; TPA, two-photon absorption. The incident excitation induces a positive transient differential transmission in sp^2 domains due to SA and a negative transient differential transmission in sp^3 domains due to TPA. The insets are the band gap structures of sp^2 domains (left) and sp^3 domains (right). The bottom shows that the combination of the transient differential transmissions corresponds to sp^2 and sp^3 domains, respectively.

can be fit to a single exponential decay with a time constant of $\tau_1 = 0.17$ ps, as shown in Figure 1e, which is comparable to reduced GO.⁶ The absence of slow decays in FGO2 further verifies that the nanosized sp^2 clusters play an important role in the relaxation with long time constant.

Figure 1b,d,f gives the measured transient responses of SGO, FGO1, and FGO2 at high pump intensity of 411 GW/cm². First, because FGO2 has less oxidation and most fractions are sp^2 -hybridized carbons, the ultrafast dynamics of FGO2 still remain a fast relaxation with a biexponential decay. The major component is a faster process with time constant τ_1 ($A_1 = 0.96$ and 0.99 for low and high pump intensity). The τ_1 of 0.25 ps is larger than that at low pump intensity due to the influence of sp^3 domains. Consequently, the oxidation at the sheet edges improves the solubility and preserves some of unique properties of the pristine graphene simultaneously.²⁷ Surprisingly, fast photoinduced absorption (PA) that has a negative signal for $\Delta T/T_0$ can be observed in the differential transmission of SGO and FGO following the PB. At this point, the triexponential decay does not fit into the complicated ultrafast dynamic process. Here we consider that nonlinear absorption (NLA) in GO contributes to PA effect.²⁸ Because the response of NLA is very fast and nearly instantaneous, it should be considered as multiphoton absorption. Direct multiphoton absorption was also found to be insignificant in graphene.²⁹ According to the energy gap structure of sp^3 domains, as shown in Figure 2, TPA is allowed at high pump intensity.

To analyze our data of SGO and FGO at high pump intensity, we consider a model for the transient response with heterogeneous photoinduced dynamics localized in sp^2 clusters and sp^3 domains, respectively. The predicted change in the transient response of GO under strong excitation arises from both sp^2 and sp^3 domains contributions, $\Delta T/T_0 = \Delta T/T_0(sp^2) + \Delta T/T_0(sp^3)$. The sp^2 term $\Delta T/T_0(sp^2)$ yields a positive contribution to the differential transmission with a relaxation of triexponential decay (τ_1, τ_2, τ_3). The photoinduced change $\Delta T/T_0(sp^3)$ from sp^3 domains is negative in sign. From Figure 1a,c, we can observe positive transient differential transmission for SGO and FGO1 due to the PB in sp^2 domains,^{4,5} which implies that the sp^2 contribution dominates at

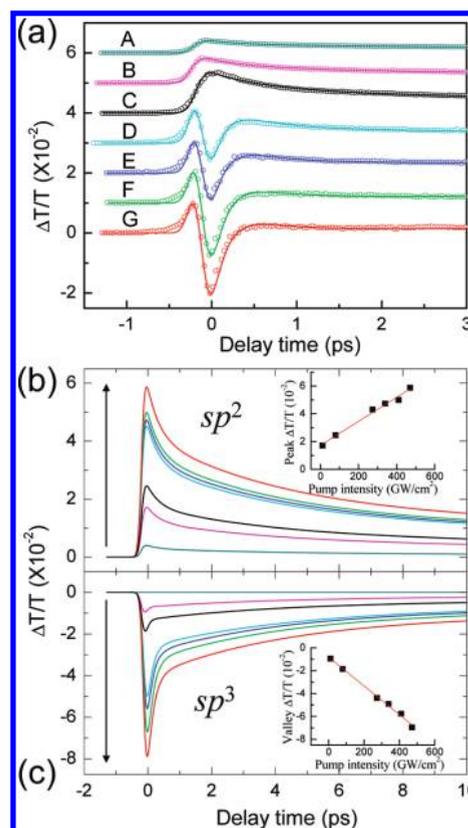


Figure 3. (a) Transient differential transmission of SGO for excitation at different pump intensities: A, 5.7 GW/cm²; B, 11.2 GW/cm²; C, 79.8 GW/cm²; D, 274 GW/cm²; E, 340 GW/cm²; F, 411 GW/cm²; and G, 471 GW/cm². (b) Separated transient differential transmission for sp^2 domains; the inset shows the peak $\Delta T/T_0$ for various pump intensities. (c) Separated transient differential transmission for sp^3 domains; the inset shows the valley $\Delta T/T_0$ for various pump intensities. The arrows in parts b and c represent the direction of pump intensities increasing for transient differential transmission curves.

comparatively low pump intensity, but the emergence of negative transient differential transmission as shown in Figure 1b,d indicates that the sp^2 contribution is overwhelmed by the sp^3 terms as the pump intensity increases. Therefore, the transient increase in absorption at high pump intensity reflects the change in optical response of sp^3 domains. The combination of sp^2 and sp^3 domains induces the complicated transient response in SGO and FGO1, as shown at the bottom of Figure 2. Through fitting the data of SGO and FGO1, we found that the relaxation in sp^3 domains is also a triexponential decay ($\tau_1', \tau_2', \tau_3'$). The value of τ_1' of SGO and FGO1 is smaller than laser pulse width of 130 fs. Two slow components of τ_2' and τ_3' may arise from excited-state absorption of sp^3 domains. Furthermore, it can be seen from Figure 1b,d that stronger negative $\Delta T/T_0$ in SGO indicates more sp^3 domains and more oxidation than in FGO1, which is consistent with the results from XRD, TGA, and Raman spectra.²⁰

To understand further the origin of the enhanced absorption (TPA), we performed the ultrafast pump–probe measurements for SGO at various pump intensities (Figure 3). With increasing pump intensity, a negative $\Delta T/T_0$ signal with fast relaxation becomes strong gradually. From Figure 3, we can see an important phenomenon that the valley at high pump intensities along with the peak at low pump intensities similarly occurred at zero pump–probe

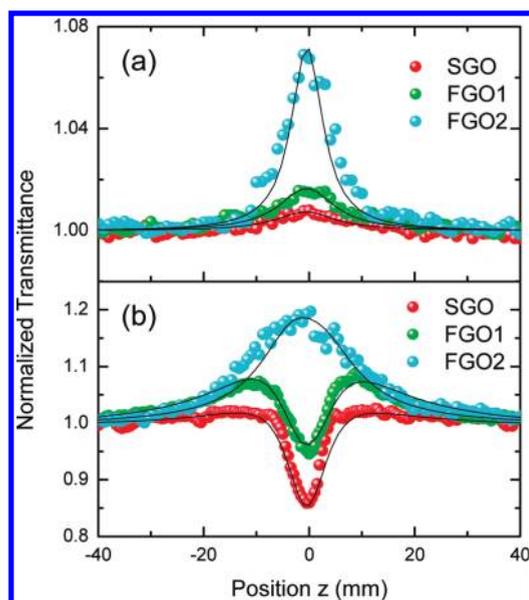


Figure 4. Open-aperture Z-scan curves of SGO, FGO1, and FGO2 at low intensity of 13 GW/cm² (a) and high intensity of 303 GW/cm² (b). The solid lines are the theoretical fits.

delay, which indicates that PB and PA are coinstantaneous. This further proves that the PA arises from sp³ domains. Moreover, the experimental data of Figure 3a can be fit (solid lines) with the same model of the heterogeneous ultrafast dynamics described above. In this fitting process, we obtained $\tau_1' < 130$ fs, $\tau_2' \approx 4$ ps, and $\tau_3' \approx 60$ ps as well as the amplitudes $A_1' = 0.68$, $A_2' = 0.21$, and $A_3' = 0.11$ for the pump intensities from B to G. Figure 3b,c gives the separated contribution from sp² and sp³ domains, respectively. We observed that the peak $\Delta T/T_0$ and the valley $\Delta T/T_0$ are proportional to the pump intensity, as shown in the insets of Figure 3. This confirms that the change in absorption of the probe is due to state filling effects and that the differential transmission is in fact proportional to the carrier density.⁶

For pristine graphene, the ultrafast carrier dynamics, combined with large absorption and Pauli blocking, make it an ideal ultrabroad band and fast saturable absorber. Figure 4 gives the normalized transmittances of SGO, FGO1, and FGO2 obtained from open-aperture Z-scan measurements.³⁰ At comparatively low intensity, GO presents a similar saturable absorption (SA) characteristic to graphene. The Z-scan curves exhibit a peak with respect to the focus, indicating that SA exists for three samples due to photoinduced bleaching. With the increasing of oxidation, the SA gradually decreases for FGO2, FGO1, and SGO. With increasing input intensity, a valley within the peak appears for SGO and FGO1 and becomes deeper with oxidation, indicating that TPA behavior occurs. The absorption coefficient in the case of the two-level system possessing inhomogeneously broadened states can be written as $\alpha = \alpha_0 / (1 + I/I_s)^{0.5} + \beta I$,³¹ where α_0 is linear absorption coefficient, I is laser intensity, I_s is saturable intensity, and β is TPA coefficient. By fitting the Z-scan curves in Figure 4b, we obtained $\beta \approx (4, 3, \text{ and } 1) \times 10^{-11}$ cm/W for SGO, FGO1, and FGO2, respectively.

These results of pump-probe and NLA measurements are consistent with our hypothesis that optical transitions in the sp² clusters and the sp³ domains of GO are independent and interrelated under different excitation. An ideal graphene sheet consists entirely of sp²-hybridized carbon atoms. In contrast, GO

is a 2D network consisting of variable sp² and sp³ concentrations, and a consequence of ordered small sp² clusters isolated with the sp³ C–O matrix is that the absorption of photons will be dispersed and localized. Thus, tuning the fraction of sp² and sp³ by careful and controllable location of specific oxygen groups presents possibilities for tailoring the optical and nonlinear optical properties of GO.

In conclusion, we have performed studies of the ultrafast dynamics and nonlinear optical responses of chemically derived GO suspension with different oxidation. The unique atomic and electronic structure of GO leads to the emergence of variable absorption processes under different input intensities, and the different absorption processes are distributed in the sp² cluster and the sp³ domains of GO. This concept suggests new possibilities for engineering linear and nonlinear optical properties on a non-stoichiometric macromolecule by manipulating the size, shape, and relative fraction of the different absorption domains. Because of the nonstoichiometric nature of GO, more information obtained via further experimental studies is necessary to understand fully the optical and electrical properties of GO.

EXPERIMENTAL SECTION

SGO was synthesized by modified Hummers method. SGO formation involves the reaction of graphite with strong oxidizers such as sulfuric acid, nitric acid, potassium chlorate, and potassium permanganate. So, it is natural to expect that FGO could be obtained by controlled oxidation/exfoliation of graphite. Thus, both the amount of oxidizers and the time for the oxidation/intercalation process play an important role in the number of layers in FGO sheets and their sizes. With fewer oxidizers or less oxidation time, both the number of layers and size of the FGO are larger. In an optimized process detailed in the Supporting Information, the mean height of fully exfoliated FGO1 was 2.5 nm, corresponding to FGO1 with three to four layers.

FGO2 was synthesized by an arc-discharge method using a buffer gas containing carbon dioxide. This method is relatively safe and inexpensive compared with techniques already reported in the literature, and more importantly, the graphene sheets have much better electrical conductivity and can be well-dispersed in common organic solvents such as DMF. The resulting FGO2 sheets have fewer defects than those (SGO and FGO1) generated using chemical methods.

SGO, FGO1, and FGO2 suspensions in DMF were centrifuged at 5000 rpm for 30 min. The concentration in DMF was 0.5 mg/mL. All suspensions were filled into a 2 mm path-length quartz cell for pump-probe and NLA measurements.

The optical pump-probe measurements were performed using a mode-locked Ti/sapphire regenerative amplifier (Spitfire Pro, Spectra Physics) with a pulse duration of $\tau_{\text{fwhm}} = 120$ fs and a repetition rate of 1 kHz at the wavelength of 800 nm. The pulse-width in our experiments was 130 fs at the sample point measured by cross correlation in a thin β barium borate crystal. The polarizations of the two pulses were kept orthogonal to each other, and a polarizer crossed with the pump polarization was placed before the detector to avoid any pump scattering. The diameters of pump beam and probe beam in sample are about 80 and 40 μm . The pump beam was modulated with the help of a chopper, and the change in probe transmitted intensity was measured with a lock-in amplifier (SR850, Stanford Research). The transient signal from DMF solvent and the decomposition of GO have been

tested at highest pump intensity used in our experiments, and no obvious influence was observed.

NLA measurements were obtained by open aperture Z-scan method. The laser system was the same as that of pump–probe measurements. The spatial distribution of the incident pulses after passing through a spatial filter was nearly Gaussian and was verified by using a CCD camera. The energy of incident beam could be altered by rotating the $\lambda/2$ plate. The laser beam was focused onto quartz cell by using a 400 mm focal-length lens with beam waist radius ω_0 of 35 μm . The reference and transmitted pulse energies were simultaneously measured by two detectors (Ophir). Neither laser-induced damage nor scattering was observed in our measurements.

■ ASSOCIATED CONTENT

S Supporting Information. Details of the preparations of GOs and numerical simulations of Z-scan. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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