Ultrafast terahertz spectroscopy of rapid carrier relaxation in graphene oxide

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Abstract: We study the distinct terahertz (THz) carrier relaxation dynamics in graphene oxide (GO). In contrast to the graphene, we observe that the photoexcited carrier relaxation in GO exhibits a peculiar non-Drude behavior.

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Chemical exfoliation methods producing graphene oxide (GO) from graphite present a promising scheme to achieve solution-processable large-area graphene synthesis and related devices [1-3]. The solution-based GO, however, inevitably contains lattice defects due to oxygen-functionalized groups that destroy the Dirac-like linear dispersion [4, 5]. Recent work has evidenced the existence of far infrared energy gap (10-50 meV), depending on the oxygen reduction process, which leads to the insulator-semimetal transitions [4]. Thus, unlike graphene, the carrier relaxation dynamics in GO are strongly influenced by recombination kinetics associated with the defect trapping, and the relaxation pathways are expected to be different from those of graphene.

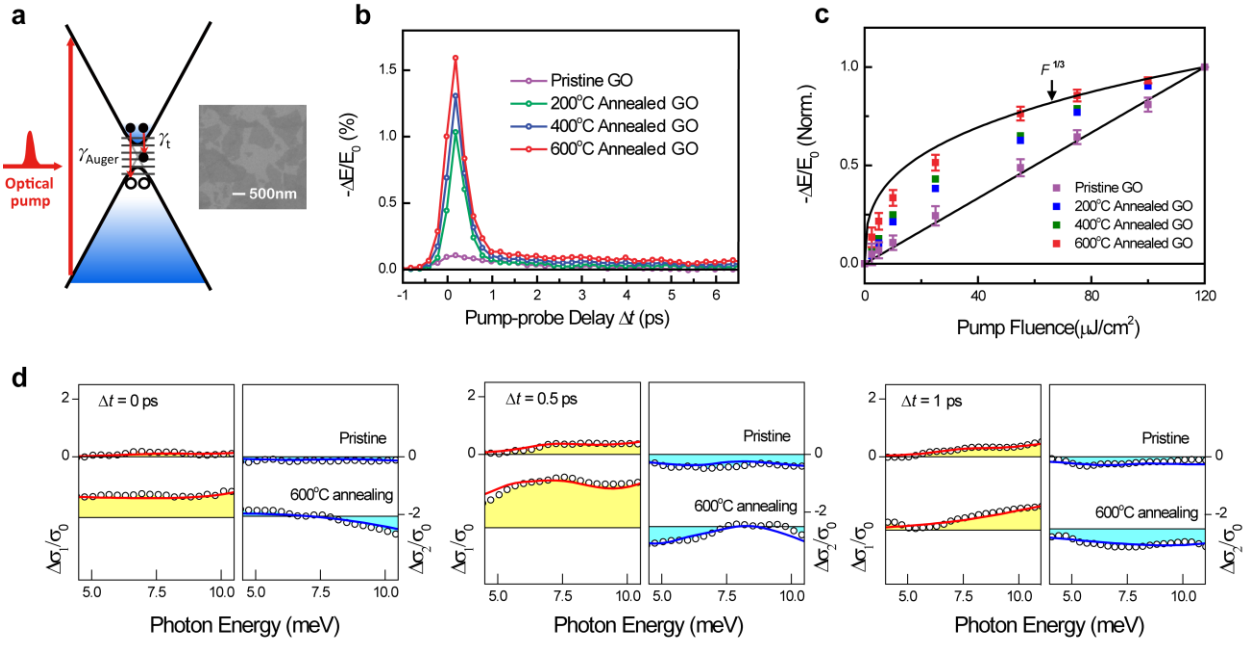

Fig. 1. **a**, Schematic of excited carrier relaxation routes in GO. Unlike pristine graphene, GO samples contain defect states in the THz ranges. **b**, The transient THz peak dynamics for various GO samples with different annealing temperature. While the dynamics of pristine GO sample presents a mono-exponential decay, the annealed GO samples displays a bi-exponential decay owing to establishing a new decay channel of Auger scattering arising from defect saturation. **c**, Peak THz amplitude as a function of F. The measured data show a one third order function of F when annealing temperature is increased. Inset: signals converted to one third order dependence of pump fluence for F > 50 μJ/cm2. **d**, Spectrally resolved THz conductivity presents defect-assisted decay in the pristine GO, and the Auger-dominant decay is enhanced by the defect saturation in the annealed GO samples representing the rapid relaxation of Drude-like free carrier response (at Δt = 0).

In GO, the defect-mediated dynamics should play a key role on the carrier relaxation pathways, yet the rapid carrier-relaxation mechanisms have not been clearly identified. For example, although recent equilibrium spectroscopies in GO have shown that the defect-assisted high-frequency absorption oscillators are distributed in the THz range [5-7], analysis on the nonequilibrium carrier relaxation dynamics (hundreds of fs decay) rely on carrier-carrier and carrier-phonon scattering of intrinsic Dirac quasiparticles [8, 9], i.e. the same characteristic dynamics of graphene appeared in exfoliated, epitaxial- or CVD-grown graphene. To date, no ultrafast carrier dynamics in GO has been reported in the THz frequency range, and the defect-trapping and recombination pathways have been barely understood.

Here, using ultrafast THz spectroscopy (Fig. 1a), we show that the photoexcited carrier relaxation in GO exhibits a peculiar non-Drude behavior [10]. As shown in the Fig. 1b, unlike graphene, the THz dynamics of GO show percolation behaviors: as the annealing temperature increases, transient THz conductivity rapidly increases and the associated carrier relaxation changes from mono- to bi-exponential decay. After saturating the recombination decay through defect trapping, a new ultrafast decay channel characterized by multi-particle Auger scattering is evidenced whose threshold pump fluence is found to be 50 $\mu J/cm^2$ as displayed in the Fig. 1c. [11] From the spectrally resolved THz responses in the Fig. 1d, we find the increased conductivity is rapidly suppressed within 1 ps due to the Auger recombination, and non-Drude THz absorptions are subsequently emerged as a result of the defect-trapped high-frequency oscillators.

In conclusion, we have investigated the kinetic origin of rapid carrier relaxation in a various set of GO samples. The pristine GO sample has a decay channel dominated by defect trapping with a mono-exponential decay, which leads to a linear F dependence. When the annealing temperature increases higher than 200 ℃, we have observed a new decay channel induced by Auger recombination. The threshold F was 50 $\mu J/cm^2$, and the peak conductivity is proportional to the cubic square root of F. The coupled rate equation including defect trapping and Auger recombination explains well the time-resolved decay dynamics. Spectrally-resolved transient THz conductivity strongly corroborates that the Auger recombination becomes dominant after saturating the defect states. We believe that these investigations will provide experimental valuables in future studies to understand the carrier relaxation dynamics in GO or in developing ultrafast GO-based optoelectronic devices.

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