Two-Terminal Graphene Oxide Devices for Electrical Modulation of Broadband Terahertz Waves


Over the last decade, major technological innovations related to graphene, single crystalline layer of hexagonally arranged carbon atoms, have transformed various research fields such as electronics, energy, and photonics. More specifically, emerging graphene optoelectronic technologies have exploited a possibility of electrical control on the interaction between electromagnetic waves and graphene. Indeed, several unique features including (i) linear and gapless energy dispersion and (ii) electrically adjustable carrier density allow graphene to be of central importance to a rapidly expanding frontier in the construction of deep-subwavelength-scaled, active photonic device for the fast and efficient modulation of broadband electromagnetic waves (e.g., from mid-infrared to terahertz (THz)).

These recent advances raise a fundamental question on how defective graphene oxide (GO), where 1–2 nm size graphene islands are surrounded by defective amorphous oxygenated domains with hydroxyl/ketone/epoxide functional groups, should be different from highly crystalline graphene particularly in terms of active control of light–matter interaction. Although a few experimental works on THz spectroscopy of GO have been recently reported, there are still neither reports on the active control of THz waves using GO nor the studies on the effect of GO complex defects on THz spectroscopy.

In this work, we aim to empirically exploit the role of GO’s complex molecular defects in electrical switching broadband THz waves transmission amplitude at room temperature. Notably, we found that the amount of the trapped charge carriers within the fully randomized, complex molecular defects (i.e., localized impurity states (LIS)) of GO can be precisely adjusted by the DC biasing with versatile and simple device architecture (i.e., a two-terminal, interdigitated electrode device); the excitation of the electrically trapped charge carrier in turn leads to a large change in broadband THz transmission (e.g., 30% at 1.0 THz). This dramatic change in broadband THz transmission (i.e., 0.3–2 THz) was achieved with a deep-subwavelength thick GO paper (500 nm) without any assistance of the foreign structural motifs (e.g., metamaterials, plasmonic structures, and Fabry–Pérot architectures).

Systematic THz spectroscopy of the chemically reduced GO further revealed the critical role of GO’s complex molecular defects in the active control of broadband THz transmission. Also, we observed the trapped charge carriers within LIS of GO can additionally provide interesting hysteretic behavior in the control of broadband THz transmission, which could be applied to the THz-based photonic memory devices.

Figure 1a–c presents schematic and macro/microscopic images of the two-terminal GO devices used in the present work. The GO device mainly consists of two functional parts: (i) GO paper (i.e., multistacked GO flakes) and (ii) two-terminal, interdigitated gold (Au) electrodes (Au microwire array) patterned on the polyimide (PI) flexible substrate (2.6 µm in thickness). High-quality monolayer GO flakes, prepared by acidic chemical exfoliation of graphite, were dispersed in deionized water; then, GO aqueous solutions were vacuum-filtered in order to obtain mechanically robust, freestanding paper platform (500 nm in averaged thickness). The transmission electron microscope image and UV–vis spectroscopy of the obtained GO flakes are summarized in Figures S1 and S2 in the Supporting Information. In particular, UV–vis spectroscopy and its Tauc plot analysis verify the presence of both energy bandgap (3.4–4.0 eV) and LIS, which makes GO contrast to graphene with zero bandgap. The mechanical robustness of the paper-type film can facilitate the transfer of GO onto any desired substrate; herein, by using solvent-assisted transfer printing (see Figure S3 in the Supporting Information), GO paper was directly integrated onto the surface of the interdigitated, two-terminal electrodes (100 nm thick Au micro wire array with 10 nm Ti adhesion layer), as shown in Figure 1b–d. Scanning electron microscope image in Figure 1d shows the large-area GO paper (1 cm × 2 cm), conformably printed onto the predeveloped electrodes. The average roughness of GO (i.e., root-mean-square) was measured about 180 nm, which is still far below the wavelength of interest (Figure S4 in the
Supporting Information). Therefore, scattering of THz wave from the rough surface of GO can be negligible. The chemical composition of the GO papers was characterized by X-ray photoemission spectroscopy (Figure 1e). Appearance of O–C–O/–OH (at 286.7 eV) and C=O (at 288.2 eV) shows successful oxidation of graphite and the atomic fractions of carbon and oxygen in GO paper, calculated by the intensity of each peak, were found to be 64.89% and 35.11%, respectively.

The electrode architecture on the PI substrate was developed by consecutive processes consisting of conventional photolithography, metal evaporation (electron beam deposition), and the liftoff processes. The width of the Au microwire electrodes was 5 µm and the gap between the two-terminal electrodes was varied between 20 and 100 µm. This two-terminal electrode structure was designed for the transparency at broadband THz waves of interest (0.3–2.0 THz), which are linearly polarized along the direction perpendicular to the grating vector of Au microwire array (referred to as THz transparent electrode), as presented in Figure S5 in the Supporting Information). More significantly, the two-terminal “interdigitated” electrode was designed to effectively increase the electrode area over the large-area GO paper, compared with a simple two-terminal device (see Figure S6 in the Supporting Information). THz time-domain spectroscopy (THz-TDS) was used to characterize the THz transmission through the two-terminal GO device. All of the THz-TDS measurements were performed at room temperature (≈15–20 °C), and the polarization of the THz wave was set to be perpendicular to the Au microwire array electrodes for the transparency at the THz frequency of interest (≈0.3–2.0 THz). Additionally, a custom-built encapsulation box for the THz-TDS setup with nitrogen gas purging provided the ability to measure the THz transmission under low relative humidity (as low as 1%), which allowed us to minimize the moisture-assisted, permanent electrochemical reduction of GO. The first subject in the present work involved assessing whether an electrical DC biasing of GO can control THz wave transmission amplitude. As described previously, the systematic THz spectroscopy analysis of GO with various levels of DC biasing was aided by the interdigitated two-terminal electrodes (20 µm gap of interdigitated electrodes). The DC bias voltage ($V_{ds}$) was quasi-statically swept from −0.1 to +0.1 V: for $|V_{ds}| > 0.1$, the permanent electrical reduction of GO occurred. The dwell time per each voltage was 250 s. Figure 2a (a negative DC biasing), b (a positive DC biasing) shows the representative control of broadband THz transmission by DC biasing of GO paper. Two important features are noteworthy. First, the THz transmission of the as-prepared GO decreases monotonically with frequency. This behavior is completely attributed to the presence of the GO. The dashed lines in Figure 2a,b show the THz transmission for the substrate...
only (i.e., without GO). As shown in Figure 2a,b, the most of the THz wave is transparent to the substrate. Thus, the THz waves are absorbed into the GO paper and this absorption increases with frequency. This behavior (monotonic decrease of transmission amplitude with THz frequency) is different from that for the reduced GO. It is well known that in the highly reduced GO, the transmission of THz wave is generally independent of frequency. More detailed underlying mechanism for this monotonic decrease of transmission amplitude with THz frequency will be discussed following the analysis of Figure 2c–f.

Second, the broadband THz transmission of GO is continuously decreased, as $V_{ds}$ is changed from 0 to −0.1 V or +0.1 V. In particular, the broadband THz transmission change by DC biasing (i.e., $\Delta T/T_{V=0}$, where $\Delta T = T_{V=0} - T$) was observed up to $30\%$ (e.g., at 1.0 THz) in the frequency range between 0.3 and 2.0 THz (for the positive DC biasing).

We then quantified the behavior of $\Delta T/T_{V=0}$ at 1.0 THz, in more depth, as shown in Figure 2c. The two distinct regimes are clearly observed: (i) steep increase of $\Delta T/T_{V=0}$ under 0.005 of $V_{ds}$ (referred to as trapping regime) and a slow increase in $\Delta T/T_{V=0}$ beyond 0.005 of $V_{ds}$ (referred to as transporting regime). Measured electrical current of GO as a function of $V_{ds}$; as with $\Delta T/T_{V=0}$, trapping and transporting regimes are obvious. Schematic trapped electrons at low bias, in which the electrons driven by DC biasing are preferably trapped within localized impurity states (LIS) at the bottom of the conduction band (i.e., below the mobility edge). Schematic for transporting regime at high bias, in which the electrons can be transported across GO beyond the saturation of LIS with electrons. Note that the impurity states at the top of the valence band are fully occupied and the majority current comes from electrons.
Metallicity is determined by the temperature dependence of the resistivity. Meanwhile, the anisotropy in electrical conduction within GO (e.g., positive DC biasing is greater than negative DC biasing) was often observed in our experimental device because of the nonuniformly distributed contact of electrodes and GO paper at the two terminals.[26] The nonidentical behaviors of the change in $\Delta T/T_0$ between positive and negative DC biasing could be attributed to this anisotropic electrical conduction of our devices. Thus, it is natural to ask, “why does DC biasing of GO resulted in a decrease in the broadband THz transmission?”

A speculative explanation derived from these observations is based on two things. (i) The DC biasing can provide electrons into the device; subsequently, the complex molecular defects of GO can trap these injected electrons within LIS (see Figure 2e). (ii) The electrons, trapped within randomly distributed LIS, can be excited to the extended region of the conduction band (or upper energy level) by broadband THz irradiation. In the present work, the bandgap energy of GO was measured to be $\approx 3.4-4.0$ eV (see Figure S2b in the Supporting Information). Thus, the bandgap of GO is nothing to do with the THz absorption (i.e., the THz absorption is not attributed to the interband transition between valence and conduction bands). Also, the nonbiased GOs, used in this study, were found to be insulators because the absorption becomes zero in the low-frequency limit; thus, it is naturally expected no Drude peak at zero frequency. In our system, the THz wave absorption decreases (or the transmission increases), as the frequency goes to zero, indicating the typical insulating behavior (i.e., disappearance of the Drude peak). Meanwhile, the long band tail in the UV–vis Tauc plot of GO aqueous solution indicates the presence of randomly distributed LIS (at the bottom of the conduction band and at the top of valence band). In the trapping regime (Figure 2f), the transporting electrons driven by $V_{ds}$ should be first accumulated into the fully randomized LIS, in that the electrical conductivity between drain and source electrodes cannot be increased significantly (see Figure 2d). The hopping current through the impurity states may dominate for $|V_{ds}| < 0.005$ V. However, the trapped electrons within LIS can be excited into the extended states of the conduction band (i.e., above the mobility edge) through broadband THz absorption, as evidenced by a significant increase in $\Delta T/T_0$ despite of negligible change in current (see Figure 2c). As $V_{ds}$ increases (especially beyond $V_{ds} = 0.005$), the trapped electrons within LIS become saturated gradually, while the electrons can be transported across the GO paper (see Figure 2f of transporting regime). This in turn results in both the increase in conductance (Figure 2d) and a saturated enhancement of $\Delta T/T_0$ beyond $|V_{ds}|$ of 0.005.

Specifically, compared with single layer graphene, the GO paper used in this study can be treated as a relatively thick, amorphous carbon layer, in which quite complex and various molecular defects such as hydroxyl/ketone/epoxide functional groups, vacancies, and the adsorbed water are fully randomized. This unique randomness of the molecular defects makes the LIS of GO paper almost continuous and broadband. Thus, in a sense, broadband THz waves can be absorbed through the excitation of the trapped electrons within nearly continuous and broadband LIS. Furthermore, the amount of the trapped electrons within the LIS of GO paper can be tuned by DC biasing, so as to achieve active control of broadband THz transmission.

The monotonic decrease of transmission (or increase of absorption) amplitude with THz frequency can also be rationalized by the electronic transition from lower impurity levels to higher impurity levels. At room temperature, the part of impurity levels near the bottom of conduction band can be occupied by the thermally excited electrons from metal contacts (i.e., thermionic effect) and/or valence band (i.e., direct thermal excitation). Since the energy difference among impurity levels is not specifically determined in THz range, the transition of the already trapped electrons at room temperature can be facilitated, as the incident THz frequency is increased. Thus, the available density of states for the transition at THz range increases with frequency. This effect, in turn, results in the increase of the THz absorption with frequency.

We next characterized the hysteretic behavior of the THz transmission change by cyclic DC biasing of GO paper, as summarized in Figure 3. As such, the relationship between trapped electrons and THz transmissions can be systematically verified in more depth. To demonstrate the hysteretic behavior of the THz transmission change by DC biasing of GO (i.e., pulse input), we measured the transmission of the two-terminal GO device at 1.0 THz during cyclic $V_{ds}$ sweep. The swept voltage sequence was as follows: First sweep from 0 to $\approx 0.1$ V, second sweep from $\approx 0.1$ to 0 V, third sweep from 0 to $+0.1$ V, and fourth sweep from $+0.1$ to 0 V. During each sweep, the THz transmission of GO was measured at fixed voltages. The dwell time per each voltage (i.e., pulse width) was 250 s. The measurement of THz transmission versus the voltage forms a hysteresis loop. The obtained hysteresis loop of THz wave transmission at 1.0 THz and the relevant current change are summarized, respectively, in Figure 3a,b; Figure 3c–h summarizes the proposed underlying mechanism for the hysteresis loop of $\Delta T$.

When the voltage decreases from 0 to $\approx 0.1$ V, the most of electrons from the electrode are trapped in the available impurity states, which gives rise to the reduction of THz transmission, because the trapped electrons absorb THz wave. For $V_{ds} < 0.005$ V all electrons from the electrode accumulate in the GO channel (Figure 3c,d), as evidenced both by the dramatic decrease in THz transmission (Figure 3a) and by negligible current (Figure 3b). Then, as this accumulation is saturated gradually, charges become transportable across the GO paper (Figure 3e), resulting in the increase in current. When the voltage increases from $\approx 0.1$ to 0 V the THz transmission decreases further instead of going back to the initial point at $V_{ds} = 0$ V (Figure 3a). This behavior can be understood from the trapped electrons, because the electrons cannot be released from the impurity sites during the negative DC biasing. Indeed, the THz transmission was found to be further reduced, during the second sweep (Figure 3a). In contrast, current showed the tendency of having back to the original point, owing to the gradually reduced DC bias (Figure 3b). The relatively weak hysteresis of current was well revealed as a direct evidence of electron trapping within LIS. After the second sweep (returning to 0 V), much more charges can be trapped within LIS of GO, compared with intrinsic GO (Figure 3f). As a result, THz transmission can
be dramatically dropped (e.g., from 96% to 64% at 1.0 THz; 33% of $\Delta T/T_{\text{initial state}}$, where $\Delta T$ is $T_{\text{initial state}} - T$) (Figure 3a).

In the reverse direction of the voltage (i.e., from 0 to +0.1 V and from +0.1 to 0 V), the potential of electrode is flipped with respect to the first and second sweeps, and the trapped electrons can be released. Especially at 0.1 V of the third sweep, the releasing process of trapped electrons (Figure 3g) can be facilitated, as evidenced by the increase in THz transmission again (see Figure 3a). Eventually, most of the trapped electrons was released during fourth sweep (Figure 3h), in that THz transmission was found to be returned almost to the original point after fourth sweep (Figure 3a). Conclusively, the complex hysteretic loop of $\Delta T$ was achieved. As well as electron trapping, the quite complex chemical and structural defects of GO possibly lead to the complicated polarization behavior, contributing to such unique hysteretic loop of $\Delta T$. This aspect needs to be more carefully investigated in the future works. Interestingly, such hysteretic characteristic allows us to further reduce the THz transmission amplitude, so as to further increase the available range of $\Delta T/T_V = 0$ (e.g., for negative DC biasing, from 18% to $\approx$ 30% at 1.0 THz).

Also, in principle, this hysteresis behavior in current versus sweep voltage can be applied to the photonic memory devices. However, for the currently available device scheme, the switching speed was found to be a relatively slow (i.e., required minimum pulse width was 250 s), when we used $-0.1$ V.
or +0.1 V as a pulse input. This mainly stems from two reasons. First, the thickness of GO used in this study was relatively thick (≈500 nm), in that the molecular defect sites within GO were incredibly huge. These huge molecular defects result in a relatively long saturation time in terms of accumulating electrons within LIS. Second, we used GO with a high amount of oxygen (≈35%); thus, GOs are easily to be electrochemically reduced, when biased by DC voltage.[24,25] Indeed, as mentioned above, GO in our device was permanently reduced beyond a relatively small pulse input (i.e., DC bias voltage of −0.1 V or +0.1 V). This limited pulse input further makes switch speed slow.

However, in turn, these huge molecular defects of GO are advantageous over graphene, in terms of the memory retention time (or durability). With the given DC bias pulse (−0.1 V or +0.1 V DC bias voltage for 250 s writing time), the memory retention time was estimated to be at least 22 h, as shown in Figure S7 in the Supporting Information. We believe that this tradeoff relation between switching speed and memory retention time could be addressed by optimizing the thickness of GO and amount of oxygen defects within GO.

Additionally, this hysteretic behavior and the range of ΔT/T0 during cyclic Vds sweep should be dependent on the effective electrical potential (i.e., effective pulse input). Indeed, the lowered electrical potential across the two-terminal electrodes (i.e., 100 μm gap of interdigitated electrodes) resulted in the reduced range of ΔT/T0 (during first and second sweeps, ∼15%), as shown in Figure 4a. This result indicates that the electron trapping and the relevant electrical control of THz transmission can be controlled by adjusting the effective electrical potential between the interdigitated electrodes. Also, generally, we observed that the hysteresis loop becomes narrower with the faster change of Vds (reduced pulse width), as similar to Figure 4a (not shown in this Communication). This dependence arises because of the dynamic lag between the carrier trapping time and sweeping time of voltage.

To further test the role of complex molecular defects in the electrical control of broadband THz transmission, we finally performed the THz spectroscopy of hydrazine (NH₂NH₂)-treated GO (HReGO).[27,28] As previously reported, the oxygen molecular defects with various bonding motifs were effectively removed from solid-state GO (see details of HReGO, presented in Figures S8 and S9 in the Supporting Information).[27] Thus, this HReGO paper, in which the number of layers is almost the same with that for the as-prepared GO paper, can be treated as a good reference to directly investigate the effect of molecular defects on the trapped electron-mediated control of broadband THz transmission. Herein, we systematically adjusted the hydrazine treatment time (20, 60, and 180 s). Figure 4b presents typical THz spectroscopic results of GO and HReGO with a controlled chemical reduction. The hydrazine treatment of GO resulted in the reduction of broadband THz transmission together with the distinctly flatten profile, because GO was significantly reduced.[22] Also, the degree of the reduction in THz transmission was proportional to the hydrazine treatment time (free carriers can be excited by intraband transitions).

More importantly, in the case of hydrazine-treated GO, the available range of ΔT/T0 during cyclic DC biasing was significantly narrowed (at 1.0 THz), as presented in Figure 4c. As with the results of Figure 3a, we carried out cyclic ΔT/T0, as following sequence: First sweep from 0 to −0.1 V, second sweep from −0.1 to 0 V, third sweep from 0 to +0.1 V, and fourth sweep from +0.1 to 0 V. For this study, we used 20 s hydrazine-treated GO, as other hydrazine-treated GO papers (the hydrazine treatment times were 60 and 180 s) were not DC biased due to the near-metallic properties (i.e., Figure S10, Supporting Information). Such significantly narrowed range of ΔT/T0 after the hydrazine treatment originated from the removed molecular defects and thus less efficient electron trapping; further elucidating the role of GO’s molecular defect in the electrical control of THz transmission.

The concept reported in the present work newly establishes a baseline for the pivotal role of GO’s complex molecular defects in DC biasing-controlled THz transmission. The THz spectroscopy of DC biased GO together with cyclic I–V measurements were systematically performed to support the possibilities for the electrical control of broadband THz transmission. Therefore, the capabilities for switching THz transmission are more accessible with the simple and efficient device architecture (the conformably printed GO paper onto two-terminal, interdigitated electrode). This generic strategy should expand the range of possible active optoelectronic devices with a broadband and large change of THz transmission. Further improvements in

![Figure 4](https://www.advopticalmat.de)

**Figure 4.** a) Representative hysteretic behavior of GO THz transmission (1.0 THz) during a cyclic DC biasing with 100 μm gap between interdigitated electrodes. Due to the much larger gap between interdigitated electrodes, the effective electrical potential was significantly reduced, compared with the results of Figure 3a. b) THz spectroscopy of GO with controlled hydrazine treatment times. As the oxygen-related molecular defects are removed from GO by hydrazine treatment, the broadband THz transmission was significantly reduced. c) Cyclic measurement of THz transmission of hydrazine-treated GO (for 20 s) during cyclic DC biasing. The gap between interdigitated electrodes was 20 μm.
the THz transmission change together with detailed investigations of switching time which will be critical for enabling practical application are possible; the potential steps in this direction include the optimization of the GO thickness, chemical composition, and device architectures.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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