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Control of the ultrafast photo-electronic dynamics of a chemical-vapor-deposited-grown graphene by ozone oxidation

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Diverse ultrafast dynamics have been reported on different graphene prepared by different methods. Chemicalvapor-deposited (CVD) growth is regarded as a very promising method for highly efficient production of graphene. However, CVD-grown graphene usually presents only one of the diverse ultrafast dynamics. Thus, control of the ultrafast photo-electronic dynamics of CVD-grown graphene is vital to present the diversity for different photodetection applications of CVD-grown graphene. In this paper, we report on the first realization to our knowledge of control of the ultrafast dynamics of CVD-grown graphene and the manifestation of diverse ultrafast dynamics on sole CVD-grown graphene. We study the ultrafast photoelectronic dynamics of CVD-grown graphene with different degrees of oxidation caused by ozone oxidation using femtosecond time-resolved transient differential transmission spectroscopy, and we find that the ultrafast dynamics can evolve obviously with the time of ozone oxidation. The diverse ultrafast dynamics reported previously on different monolayer graphenes prepared by different methods are achieved on the sole CVD-grown graphene by controlling oxidation time. The mechanism for manipulation of the ultrafast dynamics by ozone oxidation is revealed by Raman spectroscopy as the control of the Fermi level of CVD-grown graphene. Simulations of dynamics based on the optical conductivity model of graphene and Fermi level change well reproduce the observed diverse ultrafast dynamics. Our results are very important for the diverse applications of graphene and open a new path toward the diverse ultrafast dynamics on the sole graphene prepared by any method. © 2019 Chinese Laser Press

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1. INTRODUCTION

The ultrafast photo-electronic dynamics of graphene have been investigated extensively in the past decade using transient pump-probe differential transmission and reflection spectroscopy. Diverse ultrafast photo-electronic dynamics have been manifested and reported for mono- and few-layer graphene fabricated by different methods [1–19]. The manifested diverse ultrafast dynamics included fully positive differential transmission dynamics (DTD) [1–5,10,14,15,17], fully negative DTD [7–9,11], fully positive differential reflection dynamics (DRD) [12,13], and fully negative DRD [6] as well as a complex DTD that presented a strong positive peak near zero time delay followed by negative slow recovery dynamics [14–19]. We have given a possible explanation on the origin of those diverse ultrafast dynamics in graphene by computation simulations of the dynamics based on a dynamic optical conductivity model of

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graphene that we developed [18], and we found that the ultrafast dynamics of graphene were influenced by several parameters including carrier scattering time, doped density or Fermi level, and the probed level in the bands or photon energy of the probe, etc. [18]. The effect of the photon energy of the probe on ultrafast dynamics has been confirmed experimentally [14,15,17]. However, the influence of other parameters on ultrafast dynamics was seldom studied due to difficulties in controlling those parameters experimentally. In other words, the control of ultrafast dynamics of graphene by tuning Fermi level and/or carrier scattering time has not been reported to our knowledge.

In recent years, the oxidation of graphene by ozone has been studied intensively [20–24]. It was found that the oxidized process by ozone was mild, and the oxidation rate was controllable. More important was that the oxidation process was reversible

[20,23], and oxidized graphene could be reduced by ultraviolet irradiation [20] or vacuum annealing [23]. Especially important was that the mild oxidized graphene kept almost the basal plane structure of graphene, as scanning tunnel microscopy images showed in Refs. [20,23], and hence its band structure was almost the same as that of pristine graphene except for a very small bandgap opening [21,23]. It has already been reported that the degree of oxidation can tune the electrical and optical properties of graphene remarkably, such as electrical resistance and optical transmittance [22]. Then, is it possible to control the ultrafast photoelectronic dynamics of graphene by the degree of oxidation? This has not yet been reported to our knowledge. However, it is very important to realize the control of the ultrafast dynamics to meet different applications of graphene, such as ultrafast photodetectors [25] and saturable absorbers for mode-locked fiber lasers [26,27]. More important is that diverse ultrafast dynamics of graphene can be manifested on sole graphene prepared by any fabrication method if ultrafast dynamics can be controlled, whereas the presently reported diverse ultrafast dynamics were demonstrated on multiple kinds of graphene prepared by different methods, such as mechanical exfoliation, chemical vapor deposition (CVD), epitaxial growth on SiC, and reduction of graphene oxide. In other words, it is possible to realize that the diverse ultrafast dynamics of graphene are independent of preparation methods. In this way, the preparation method with the highest production efficiency can always be favored.

In this paper, we explore the manipulation of the ultrafast dynamics of CVD-grown monolayer graphene by ozone oxidation, and we find that the ultrafast dynamics can indeed be controlled by oxidation time. The ultrafast DTD can evolve from initial complex DTD to final fully positive DTD, while the fully positive DTD is ideal for ultrafast photodetection applications of graphene. Optical characterizations of oxidized graphene by Raman spectroscopy reveal the maintenance of basal structure and Fermi level change of graphene. As a result, the manipulation of ultrafast dynamics originates from the tuning Fermi level of the CVD-grown graphene by ozone oxidation, agreeing well with computation simulations of ultrafast dynamics.

2. SAMPLE AND EXPERIMENTAL SETUP

Our samples are monolayer graphene grown on Cu foil by the CVD method [28] and then transferred on quartz substrates. Six similar monolayer graphene samples are transferred to quartz substrates. Then, five of them are placed into ozone flow produced by flowing oxygen gas through an ozone generator [22]. They are oxidized at a substrate temperature of 90°C for 2, 4, 6, 8, and 10 min, respectively. The details of oxidation processing of graphene have been described elsewhere [22].

A Ti:sapphire self-mode-locked oscillator is used to study ultrafast carrier dynamics using transient differential transmission spectroscopy. The mode-locked laser pulse train has a repetition rate of 94 MHz, a tunable central wavelength from 750 to 850 nm, and a duration of ~80 fs. The laser pulse goes through a standard pump-probe setup and is split into a strong pump and a weak probe with a pump-to-probe intensity ratio larger than 10. The focused spot size of the pump and probe is about 50 μ m in diameter and overlapped on the sample. The pump and probe are perpendicularly polarized so that a polarization analyzer can be placed in front of photodetector to filter out the scattered pump light into the probe. The pump beam is modulated at a frequency of about 1.34 kHz by an optical chopper whose output electrical pulse synchronizes a lock-in amplifier. Transient transmission change of the probe through the graphene is detected by a Si photodiode and measured by the lock-in amplifier. The schematic of our experimental setup can be found in Ref. [29], but the transmission grating in front of the sample needs to be removed for our experiments.

3. RESULTS

A. Excitation Power Dependence of Ultrafast Dynamics of Pristine Graphene

The ultrafast dynamics of pristine monolayer CVD-graphene are first studied under the excitation of different pump powers. Excitation power-dependent ultrafast dynamics are plotted in Fig. 1. They are the same as what we reported previously in Refs. [18] and [19], and they present a first positive peak near zero time and then sharply decay down to a negative minimum followed by negative slow recovery dynamics toward the initial background. The positive peak and negative minimum enhance with increasing pump power as shown in Fig. 1. Such consistent ultrafast dynamics show the excellent repeatability and stability of the CVD-grown method and the photoelectronic properties of CVD-grown graphene.

B. Effect of O_3 Oxidation on the Ultrafast Dynamics of Monolayer Graphene

Next, the ultrafast dynamics of CVD-grown monolayer graphene oxidized by ozone for different amounts of time are studied using the same transient differential transmission spectroscopy as described in Fig. 1. The ultrafast dynamics of five samples with different degrees of oxidation are taken and plotted in Fig. 2 for different excitation powers. The ultrafast dynamics of the sample with 2 min slight oxidation are not



Fig. 1. Pump power dependence of ultrafast differential transmission dynamics (DTD) of pristine monolayer CVD-grown graphene. The arrow points to the pump power increase.



Fig. 2. Excitation power-dependent ultrafast dynamics of oxidized graphene with different degrees of oxidation. Oxidized for (a) 4 min, (b) 6 min, (c) 8 min, and (d) 10 min.

shown in Fig. 2 due to their similarity to the ones shown in Fig. 1 and layout limitations in Fig. 2. One can see from Fig. 2 that they have a common feature: a strong positive peak near zero delay time reflecting the strong state filling of pumpinjected non-thermal carriers. The positive peak enhances monotonously with excitation power. However, they also have distinct differences: different decayed depth of the positive peak. One can see that Fig. 2(a) is similar in profile shape to Fig. 1 except that the decayed depth of the positive peak is smaller in Fig. 2(a) than in Fig. 1. However, Figs. 2(b)-2(d) look distinct in profile shape from Fig. 1. The positive peak does not sharply decay down to a negative minimum, not crossing over the zero baseline but rather sharply down to some positive extrema followed by positive slow recovery dynamics toward the initial background. The positive extremum increases with the excitation power. To exhibit the manipulation of ultrafast dynamics by oxidation more clearly, we plot the ultrafast dynamics of all samples oxidized for different amounts of time together in the same figure. Figure 3 just shows such an evolution of the ultrafast dynamics for two typical different excitation powers, a lower 28 mW and a higher 131 mW. One can discern clearly that they all contain a strong positive peak near zero delay time, and the peak's height is almost the same or only changed weakly for the same excitation power, but it increases with excitation power. The distinct difference occurs in the falling depths of the peaks. For pristine graphene without oxidation, the peak has a maximum falling depth and sharply decays down to a negative minimum followed by negative slow

recovery dynamics toward the initial background. However, the negative minimum increases gradually with increasing oxidation time, and it approaches zero as oxidation time lengthens to 4 min as the red line shows in Fig. 3. The negative minimum becomes a positive maximum followed by slow positive recovery dynamics as oxidation time lengthens to 6 min and longer as the blue, green solid line and magenta dashed lines show in Fig. 3. In other words, ultrafast dynamics become a fully positive DTD as oxidation time reaches 6 min and longer. One can also see that the ultrafast dynamics are almost identical for 8 min and 10 min, which may imply the saturation of the oxidation of graphene. In one word, oxidation time can control the sharp falling depth of the positive peak near zero time, and the ultrafast dynamics evolve from the initial complex DTD of pristine graphene to fully positive DTD with increasing oxidation time. Such ultrafast dynamic evolution clearly reveals the controllability of ultrafast dynamics of graphene by means of ozone oxidation.

Ultrafast dynamics are actually the impulse response function of graphene to irradiation photons. The ultrafast and monotonous decay impulse response function is preferable for ultrafast photodetection applications of graphene. As a result, the ultrafast dynamics of CVD-grown graphene oxidized between 4 and 6 min are the best impulse response function for ultrafast photodetection applications of CVD-grown graphene as the red and blue lines show in Figs. 3(a) and 3(b). With such an impulse response, graphene photodetectors may have a maximum cutoff frequency close to terahertz (THz).



Fig. 3. Oxidation time dependence of the ultrafast dynamics of six graphene samples under excitation power of (a) 28 mW and (b) 131 mW.

4. DISCUSSION

A. Mechanism of Ozone-Oxidized Manipulation of Ultrafast Dynamics of Graphene

It is well known that the ultrafast transmission dynamics of graphene are controlled by its optical conductivity. The optical conductivity contains two parts. It can be written as [7,13]

$$\frac{\operatorname{Re}[\sigma(\omega)]}{\sigma_0} = \frac{4k_B T}{\pi\hbar} [\ln(1 + e^{E_F^{\flat}/k_B T}) + \ln(1 + e^{E_F^{\flat}/k_B T})] \frac{1/\tau}{\omega^2 + 1/\tau^2} + \frac{1}{2} \left[\tanh\left(\frac{\hbar\omega - 2E_F^{\flat}}{4k_B T}\right) + \tanh\left(\frac{\hbar\omega - 2E_F^{\flat}}{4k_B T}\right) \right],$$
(1)

where $\sigma_0 = e^2/(4\hbar)$ is the universal quantum conductivity. τ is the momentum scattering time. $E_F^e(E_F^h)$ is the electron (hole) Fermi energy with the relation $E_F^e = -E_F^h$ under thermal equilibrium condition. k_B and T are the Boltzmann constant and absolute temperature, respectively.

In Eq. (1), the term in the first square brackets describes intraband absorption. The second part in the last square brackets describes interband absorption. Intraband absorption makes a negative contribution to DTD, whereas interband absorption makes a positive contribution to DTD. Therefore, total DTD reflects the competition between intra- and interband absorptions as we have discussed previously [18]. As shown in Fig. 3,

oxidation mainly leads to weakening of the negative signal in DTD, which implies the weakening of the intraband absorption contribution. One can see from Eq. (1) that intraband absorption is indirectly proportional to momentum scattering time (τ) and Fermi level (E_F). As a result, increasing τ and E_F can weaken the negative signal in DTD. Figure 3 shows that the negative signal weakens with lengthening oxidation time, which implies that ozone oxidation may mainly manipulate τ and/or E_F . However, it is easy to rule out the main manipulation of τ because τ can only reduce, rather than increase, with increasing oxidation time. As pointed out in Refs. [21,23], ozone oxidation mainly leads to the formation of epoxide groups in the graphene basal plane, which gives rise to the enhancement of momentum scattering due to additional electrondefect scatterings (epoxide groups being equivalent to local defects in graphene). In this way, momentum scattering time τ can only decrease, instead of increasing, which leads to the enhancement of the negative signal in DTD [18]. It disagrees with the experimental fact that the negative signal in DTD weakens with lengthening oxidation time as shown in Fig. 3. Therefore, the main manipulation of τ induced by ozone oxidation can be ruled out because the time of electron-electron scatterings is much less than that of electron-defect scatterings. The only remaining parameter manipulated by ozone oxidation is Fermi level E_F .

To understand the Fermi level change of oxidized CVDgrown graphene, we carry out optical characterization of oxidized graphene samples by Raman spectroscopy. Figure 4 shows the evolution of the Raman spectrum of graphene with oxidation time. On one hand, one can see the persistent existence of a strong G peak with the oxidation, which implies the maintenance of the basal plane structure of graphene. Meanwhile, one can also discern that the D and D' peaks enhance non-monotonously with oxidation time, but the 2D peak weakens almost monotonously. Those features agree well with those reported in Refs. [22–24]. The D peak reflects the occurrence of non-sp² disordered defects induced by the



Fig. 4. Raman spectra of graphene with different amounts of oxidation time. The number over each spectrum denotes oxidation time. Each spectrum is shifted upward for clarity. The inset shows the shift of the G peak and Fermi level with oxidation time.

formation of epoxide groups on the basal plane of graphene [23], while the D' peak originates from the disordered defectinduced intravalley resonance Raman scattering [23]. The occurrence of the D' peak makes the G peak look split. Furthermore, the 2D-to-G peak intensity ratio decreases obviously with the enhancing degree of oxidation, whereas the D-to-G peak intensity ratio increases obviously, which agrees very well with the reports in Ref. [22]. On the other hand, one can see that G peak red-shifts obviously with enhancing oxidation. The accurate position of the G peak is extracted by multi-Lorentzian function fitting to each Raman spectrum, and it is plotted in the inset of Fig. 4 as a function of the oxidation time as the open squares show. Das et al. reported that the G peak of graphene shifted with a dopant density [30] and built up a corresponding relation between the position of the G peak and a dopant electron density or Fermi level. Based on the corresponding relation, the shift of the G peak induced by ozone oxidation can be converted into a shift of Fermi level of oxidized graphene as the red filled circles show in the inset of Fig. 4. One can see from the inset that the Fermi level of graphene indeed shifts with an increase of the degree of oxidation from the initial ~ 0 to ~ 0.4 eV.

B. Simulations of the Ultrafast Dynamics of Oxidized Graphene

Based on the evolution of Fermi level and the optical conductivity model in Eq. (1), we simulate the evolution of the ultrafast DTD of graphene with oxidation time or Fermi level. Figure 5 shows the evolution of the simulated ultrafast dynamics with Fermi level. In the dynamic simulation, the dynamics of the electron temperature are assumed to decay biexponentially [1,4,9,11,12,14], $T(t) = T_0 + \Delta T_1 \exp(-t/\tau_{th}) + \Delta T_2 \exp(-t/\tau_{cool})$, where τ_{th} is a time constant that measures the ultrafast thermalizing process of pump-injected carriers, while τ_{cool} describes the cooling time of the thermalized electron-optical phonon system. ΔT_1 denotes the initial temperature of the injected electrons, while ΔT_2 describes the initial temperature of the thermalized electron-optical phonon system. The dynamics of the Fermi energy are described by the dynamics



Fig. 5. Simulated ultrafast dynamics of graphene with different Fermi levels but the same other parameters.

of electron-hole recombination based on the formula [7,13] $E_F^e(t) = \hbar v_F \sqrt{\pi [N_0 + n_{ex} \exp(-t/\tau_r)]}$, where v_F is Dirac fermion velocity, N_0 is the doped electron density in graphene and corresponds to static Fermi level E_f , while n_{ex} and τ_r are the photo-injected electron density and lifetime of the electron-hole recombination, respectively. The details of these simulations have been described elsewhere [18]. The time constants used in the simulations, $\tau_{th} = 0.12$ ps, $\tau_{cool} = 1.8$ ps, and $\tau_r = 1.2$ ps, are taken from the literature [1,7]. The momentum scattering time $\tau = 0.35$ fs is used and taken from Ref. [18].

One can see from Fig. 5 that ultrafast dynamics indeed evolve obviously with Fermi level. The main change is the weakening of the negative signal in DTD with the increase of Fermi level, which agrees well with Fig. 3, although only one parameter (E_f) is changed in the simulation. This reveals that the dominant effect of ozone oxidation on graphene is indeed the manipulation of the doped electron density or the Fermi level of graphene. This conclusion is also supported by the reported metal-insulator transition induced by ozone oxidations [21,22]. Ozone oxidation mainly led to the formation of epoxide groups in the graphene basal plane [21,23]. Those epoxide groups can capture electrons from the conduction and valence bands. The density of the epoxide groups increases with ozone oxidation time, which leads to more electrons trapped in the higher density of the epoxide groups. As a result, the Fermi level in the bands increases with ozone oxidation time. Based on such a physical picture, ozone oxidation actually should give rise to a p doping in graphene [24] and makes the Fermi level of a hole in the valence band rise from the initial 0 to around 0.4 eV, although Raman spectroscopy cannot identify the type of doping.

It is worth emphasizing that Fermi level rising agrees with the resistance increase reported in Refs. [21] and [22] with oxidation time lengthening, rather than contradictory to each other. The epoxide groups formed by ozone oxidation can result in the simultaneous occurrence of two effects: p doping of graphene due to electrons in the valence band trapped in the epoxide groups and electron-defect scatterings that obstruct the transport of free charges. The p doping can enhance electrical conductivity of graphene or reduce resistance, whereas the electron-defect scatterings can hinder the transport of free charges, leading to the increase of resistance. Consequently, the real resistance of graphene depends on the competition between resistance changes induced by the two effects. In a lightly oxidized phase, a lower density of epoxide groups does not lead to obvious electron-defect scatterings, but a weak p doping can cause obvious resistance reduction and thus lead to the decrease of real resistance as reported in Ref. [22]. Contrarily, with the increase of the degree of oxidation, which leads to the higher density of epoxide groups, the resistance rising induced by electron-defect scatterings is much faster than the resistance falling induced by p doping. As a result, the real resistance increases quickly with lengthening oxidation time as reported in Ref. [22]. Eventually, the oxidized graphene can become Anderson insulators [21,22] when the oxidation content approaches saturation. It is also worth noting that Anderson insulators are different from conventional insulators, with a wide gap and fully filled valence and fully empty conduction bands.

22 Vol. 8, No. 1 / January 2020 / Photonics Research

5. CONCLUSIONS

We have explored the manipulation of ultrafast dynamics of CVD-grown graphene by ozone oxidation, and we successfully achieved control of the ultrafast dynamics by controlling the amount of ozone oxidation time. Ultrafast DTD of pristine CVD-grown graphene has a complex profile shape; it presents a strong positive peak near zero delay time, and then sharply decays down to a negative minimum followed by negative slow recovery dynamics toward the initial background. However, the ultrafast DTD can evolve from the complex profile shape to a fully positive monotonously decayed ultrafast DTD with an increase in the degree of oxidation of graphene or oxidation time exposed to ozone. The negative signal in the ultrafast DTD becomes weaker and weaker with lengthening oxidation time until it entirely disappears when oxidation time is longer than 4 min. The fully positive ultrafast DTD with an oxidation time between 4 and 6 min is an ideal impulse response function to the applications of ultrafast photodetectors of graphene. Ultrafast graphene photodetectors with such an ideal impulse response function can have a cutoff frequency close to THz. Dynamic simulations based on the optical conductivity model of graphene reveal that the mechanism of ozone oxidation manipulation of ultrafast dynamics of graphene originates from the dominant effect of ozone oxidation on the Fermi level of graphene. Further Raman spectroscopy characterization reveals the red-shift of the G peak with increasing oxidation time, supporting that ozone oxidation mainly affects the Fermi level of graphene. Our results are very important and open a new path toward the preparation-method-independent diverse ultrafast dynamics of graphene. In other words, we can achieve diverse ultrafast dynamics on monolayer graphene prepared by any method, which makes it possible to always select the most efficient preparation method due to the post-ozone-oxidation controllability of ultrafast dynamics and optical/electrical properties of graphene.

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