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# Ultrafast Transient Absorption Spectroscopy of Inkjet Printed Graphene and Aerosol Gel Graphene Films: Effect of Oxygen and Morphology on Carrier Relaxation Dynamics

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## ABSTRACT

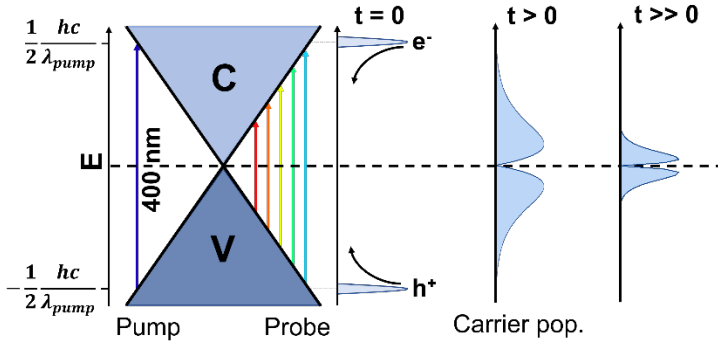
The tunable electronic properties of nano structured graphene makes it one of the most sought alternatives to metals for novel technological applications. In particular, the ability to prepare inks out of these nano structures allows for printable and thus scalable graphene-based electronics. Here we investigate the electronic properties of novel ink-jet printed aerosol gel graphene (AG) films

and compare them to that of ink-jet printed graphene (G) films. More specifically, we report on the photoinduced carrier dynamics of these materials via ultrafast transient absorption spectroscopy. In comparison to graphene, AG films have higher oxygen content as well as a complex 3D morphology. While G and AG both differ in composition and structure, the simultitude in their carrier-optical phonon (C-OP) scatter rates (in 74 – 140 fs range) indicates comparable lattice defect density. It is therefore not the number of defects but the type of defect that is electronically relevant. Indeed, in comparison to G films, which exhibit complete recovery of the transient signal, the AG films exhibit only partial recovery within our 400 ps experimental time window. The persisting signal is assigned to trapped electronic states. These long-lived electronic states are most probably due to the presence of oxygen rather than due to the films' unique 3D morphology.

## 1. INTRODUCTION

The unique two-dimensional honeycomb structure of graphene gives rise to equally unique electronic and optical properties. Graphene is a zero-bandgap semiconductor with a linear energy dispersion curve and as such, the band structure is often represented as two cones touching at the Dirac point, as depicted in Figure 1.<sup>1,2</sup> Given graphene's unique mechanical and electronic properties, many have proposed to use it in various applications ranging from ultrafast electronic devices to chemical sensors.<sup>1-5</sup> In most cases, the performance of such applications is dependent on the carrier dynamics (carrier-carrier and carrier-phonon scattering, for example), especially carriers at energies well above the ambient lattice temperature. For example, in some devices the charge transport is determined by the transient conductivity of hot carriers, well above the Fermi level. Therefore, understanding the relaxation of hot carriers is of paramount importance for device

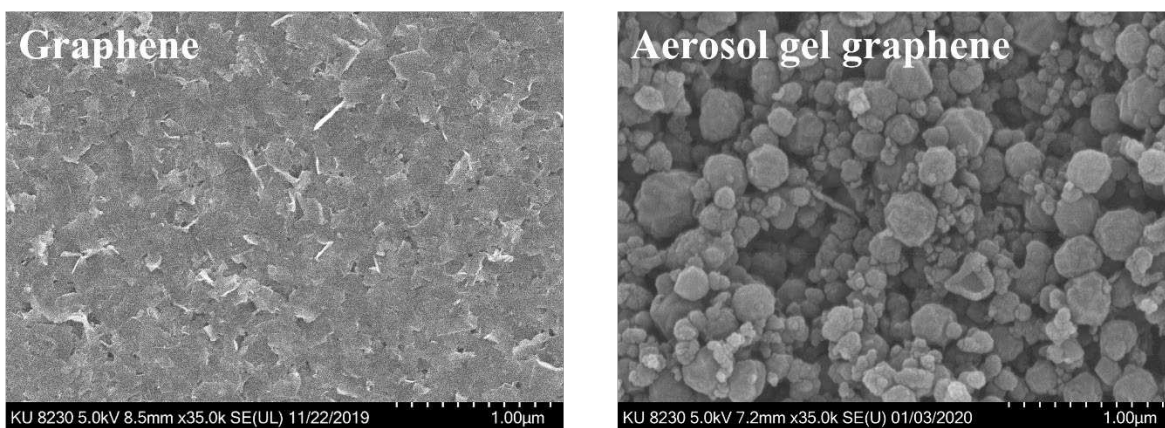
development.<sup>6</sup> However, such carrier dynamics takes place on ultrafast time scales; in the femto- to picosecond range. Accordingly, ultrafast spectroscopy is best suited to investigate the photoinduced carrier dynamics that are relevant to graphene’s performances.<sup>7-9</sup> Dawlaty et al. pioneered using degenerate pump-probe spectroscopy to measure the carrier relaxation dynamics in epitaxial graphene.<sup>10</sup> Epitaxial graphene was shown to exhibit lifetimes of 70 – 120 fs for carrier-carrier (C-C) scattering and 0.4 – 1.7 ps for carrier-phonon (C-OP) scattering. With the aim of tuning graphene’s electronic properties, various graphene-based materials have been produced and characterized via ultrafast spectroscopy. One of the most promising materials for large scale applications such as energy storage devices and sensors is graphene with a highly crumpled structure.<sup>11-14</sup> The carrier dynamics of this type of graphene aerosol gel is, however, lacking understanding. We therefore propose to address the gap of knowledge by investigating this novel and promising material via ultrafast pump-probe spectroscopy.



**Figure 1.** (Left) The band structure of graphene, with the colored arrows depicting the interaction of the pump and the probe laser pulses with the electronic structure of graphene. (Right) Evolution of the carrier (electron and hole) populations as a function of pump – probe delay,  $t$ , and energy,  $E$ .

In this work, we thus report the first ultrafast pump-probe spectroscopic study of AG films. This study focuses on photoinduced carrier dynamics and complements the previously reported chemical and morphological characterization of AG inks.<sup>11</sup> In the latter work the authors

emphasized the significant structural differences between standard graphene ink and AG ink. More specifically, it was shown that, while typical graphene ink corresponds to a suspension of 2D graphene flakes, the AG ink contains a mixture of quasi-3D (crumpled 2D flakes) and 2D graphene flakes, as shown in Figure 2. In addition to the differing morphology, the AG ink is also found to have higher oxygen content.<sup>11</sup> Therefore, the present study aims at distinguishing which of the two, changes in morphology or oxygen content, is most affecting the graphene's carrier dynamics.



**Figure 2.** SEM images of representative samples of graphene ink flakes (left) and aerosol gel graphene ink flakes (right).

The carrier dynamics are here investigated by means of ultrafast spectroscopy in transmission mode. The transmission of light through graphene is generally determined by the interband absorption (Figure 1). Interband absorption is proportional to the carrier occupation probability in the conduction band ( $c$ ),  $f_c(E)$ , and the valence band ( $v$ ),  $f_v(E)$ , at a given energy,  $E$ , above and below the Dirac point.<sup>6</sup> The carrier occupation is determined by the Fermi function and the density of states, which is a linear dispersion function for pure graphene. Excitation with a pump pulse of wavelength,  $\lambda_p$ , will produce a non-equilibrium distribution of carriers at an energy of  $hc/2\lambda_p$ , above and below the Dirac point (Figure 1). These carriers will first thermalize through ultrafast C-C scattering, with rates reported between 0.2 – 40 fs.<sup>15,16</sup> Given the sub 40 fs nature of C-C scattering,

we are not expecting to monitor carrier thermalization because it falls below our  $\sim 100$  fs time resolution. But we do expect to monitor all of the subsequent carrier cooling, via C-OP scattering, lattice cooling, trapped state formation and final charge recombination.

## 2. EXPERIMENTAL METHODS

### 2.1 Preparation of the graphene and oxygen-containing aerosol gel graphene films

The graphene ink was synthesized from graphite powders (Millipore Sigma) using a slightly modified protocol. In brief, pure graphene ink was synthesized with a high shear force using graphite powder (Millipore Sigma). A similar strategy was followed to synthesize AG ink, but the starting material was produced following a gas phase hydrocarbon and oxygen co-detonation process.<sup>11</sup> The graphene and AG inks were inkjet printed as a 0.5 by 0.5 square centimeter pattern, onto quartz substrates, each with three different thicknesses, referred to as G1, G2, G3 and AG1, AG2 and AG3, respectively. The numbering refers to the number of printing passes. Accordingly, the films thicknesses increase from 1 to 3.

### 2.2 UV-Vis spectroscopy

UV-Vis absorption measurements were taken using an Agilent Cary 60 UV-Vis spectrometer.

### 2.3 Pump-probe spectroscopy

UV-Vis pump-probe spectroscopy experiments were performed in the Lord Porter Ultrafast Laser Laboratory (ULS), The University of Sheffield, using a Helios system (HE-VIS-NIR-3200) provided by Ultrafast Systems. A Ti:Sapphire regenerative amplifier (Spitfire ACE PA-40, Spectra-Physics) provides 800 nm pulses (40 fs FWHM, 10 kHz, 1.2 mJ). The 400 nm pump pulses (2.5 kHz, 0.2  $\mu$ J) were generated through frequency doubling of the amplifier fundamental. The pump was focused onto the sample film to a beam diameter of approximately 275  $\mu$ m. The white

light probe continuum (440 – 700 nm) was generated using a sapphire crystal and a portion of the amplifier fundamental. The intensity of the probe light transmitted through the sample was measured using a CMOS camera, with a resolution of 1.5 nm. Prior to generation of the white light, the 800 nm pulses were passed through a computer controlled optical delay line (DDS300, Thorlabs), which provides up to 8 ns of pump-probe delay. The instrument response function is approximately 100 fs, based on the temporal duration of the coherent artifact signal from the quartz substrate. All steady state and time-resolved spectroscopic data was processed using OriginPro. Preprocessing of the pump-probe data was performed using SurfaceExplorer, the software package provided by Ultrafast Systems. Kinetic traces from the pump-probe data were fit in OriginPro, using a sum of decaying exponential functions convoluted with a Gaussian function. The Gaussian function was used to model the instrument response growth of the transient signal. The function can be found in the supporting information (SI).

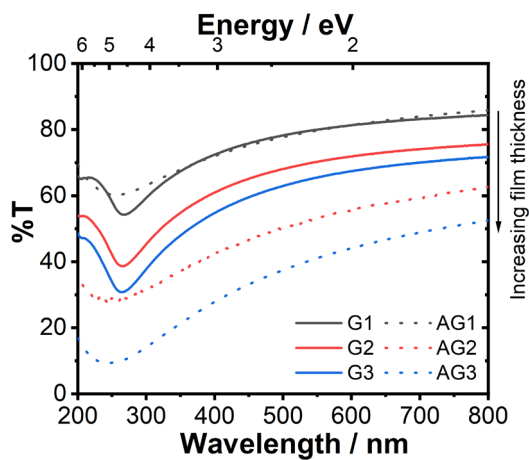
### 2.3 Theoretical calculations

Simulations of the UV-Vis absorption spectra of graphene and graphene doped with oxygen were performed using SIESTA software. Modelling details can be found in the SI.

## 3. RESULTS AND DISCUSSION

The steady state optical transmission of the graphene and AG films are shown in Figure 3, for three different film thicknesses (1, 2 and 3 printing passes). In addition, steady state Raman spectra of representative graphene and AG inks are given in the SI, Figure S1. As previously reported, graphene films are characterized by broad absorption between 200 – 800 nm, with a minimum in the transmission spectrum at 267 nm.<sup>17-19</sup> Based on this literature, the peak is assigned to a  $\pi \rightarrow \pi^*$  electronic transition of the graphene. The AG films also display broad absorption over the same

spectral region. However, the minimum in the transmission spectrum is broadened and blueshifted to  $\sim 247$  nm.



**Figure 3.** UV-Vis transmission spectra of graphene films (G, solid) and aerogel graphene films (AG, dashed) printed on quartz.

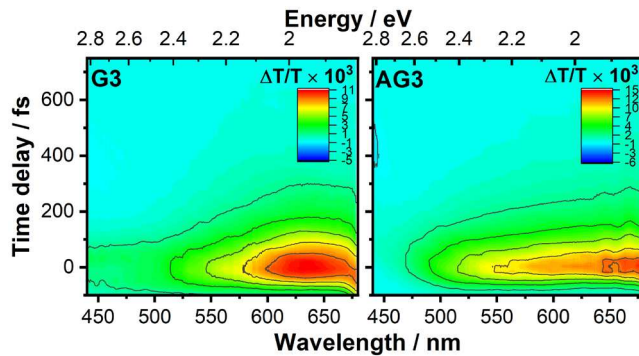
Similar blueshift in the  $\pi \rightarrow \pi^*$  peak of graphene oxide relative to the same peak in reduced graphene oxide was already reported.<sup>18</sup> In addition, our DFT calculations of the ground state electronic absorption spectrum graphene doped with oxygen shows a broadening of the  $\pi \rightarrow \pi^*$  peak, when compared to the calculated spectrum of pure graphene (see the SI, Figure S2). Similar modelling of bent graphene sheet also shows broadening of the ground state electronic absorption spectrum with its peak shifted to the red. Accordingly, while the broadening could be the result of both, the presence of oxygen and the unique 3D structure of AG, the blue-shifted UV-Vis spectra is a signature for the presence of oxygen. As illustrated by Table 1, the progressive increase in film thickness results in reduction of the transmission of the incident light. Assuming that one layer of graphene absorbs 2.3 % of incident white light,<sup>20</sup> the approximate number of layers in the graphene and AG samples have been estimated and are given below in Table 1.

**Table 1.** The %T values and the estimated number of layers for the G and AG films.

Films	%T (800 nm)	No. of layers <sup>a</sup>
G1	84.4	7
G2	75.6	12
G3	71.6	14
AG1	85.9	7
AG2	62.6	20
AG3	52.4	28

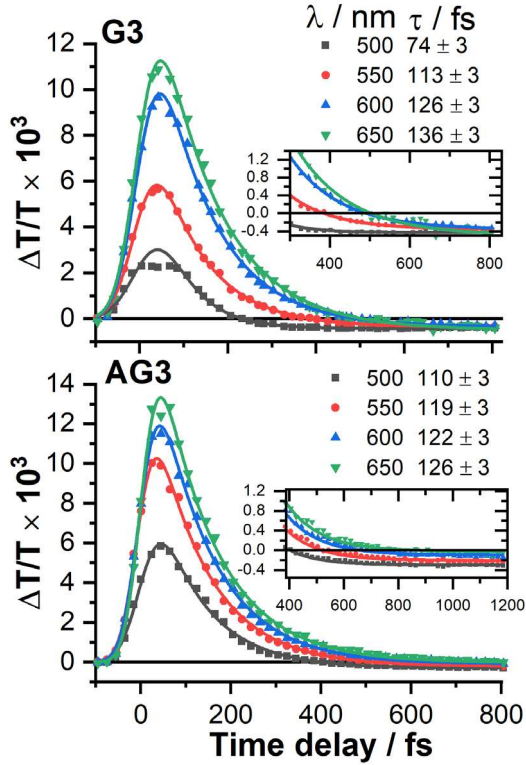
<sup>a</sup>The number of layers is derived from each sample's absorption at 800 nm.

The transient change in transmission ( $\Delta T/T$ ) of all the graphene and AG samples were measured, following excitation with a 400 nm laser pulse (0.2  $\mu\text{J}$ ). The  $\Delta T/T$  signal acquired from G3 and AG3 are shown in Figure 4. There was minimal dependence of the  $\Delta T/T$  signal dynamics on the film thickness. Therefore, the transient data for G1, G2, AG1 and AG2 are not presented in the main text but can be found in the SI (see Figure S3 to S6). Following excitation, all the films display a broad positive signal which rises within the instrument response, reaching maximum values at  $\sim 40$  fs. Because this rise time is constant across the probed range, it suggests that a hot carrier distribution is obtained within the instrument response (100 fs).



**Figure 4.** (left) The change in transmission ( $\Delta T/T$ ) of G3, following excitation at 400 nm, in the spectral range 440 – 680 nm, from -100 to 750 fs. (right) The change in transmission ( $\Delta T/T$ ) of AG3, following excitation at 400 nm, in the spectral range 440 – 680 nm, from -100 to 750 fs.

The initial positive signal is assigned to photobleaching of the broad ground state absorption due to depletion of the available valence to conduction band electronic transitions (i.e. Pauli blocking). Prompt loss of the initial signal is then observed for all the films. This behavior is exemplified by the kinetics traces of both G3 and AG3, shown in Figure 5. In the 50 – 500 fs time range, the decay of the initial bleach signal in the region from 500 to 650 nm, reveals decay lifetimes in the range of 74 – 136 fs for G3 and 110 – 126 fs for AG3. Similar loss of the initial positive  $\Delta T/T$  signal of graphene films has already been previously reported.<sup>10,15,21</sup> Such behavior has been attributed to cooling of the photogenerated carriers via C-C and C-OP scattering. Kinetic analysis reveals a linear increase in the extracted lifetime as the probe photon wavelength is increased (see supporting information, Figure S7). This demonstrates that carriers at higher energies lose their energy more rapidly compared to carriers with lesser energy and results from the increasing intraband C-OP scattering rate when the carrier energy increases.<sup>22–24</sup> Such behavior suggests that the carrier scattering corresponds mainly to intervalley scattering with K and K' optical phonons.<sup>24,25</sup>

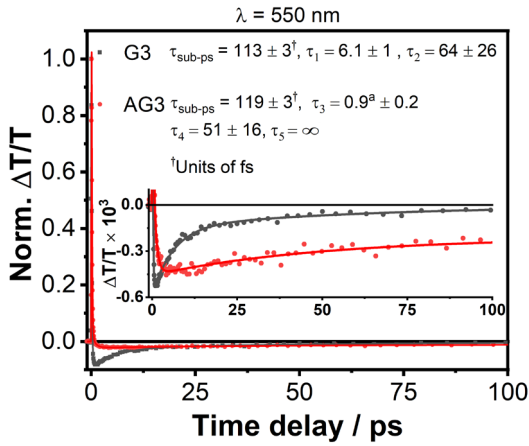


**Figure 5.** Single point kinetics traces for G3 (top) and AG3 (bottom) overlaid with their exponential fits. The associated decay lifetimes are given alongside the wavelength's legend.

Defects have also been shown to play a significant role in the initial carrier cooling of graphene. In particular, defect-induced supercollision cooling provides the additional momentum needed to satisfy conservation restrictions.<sup>26,27</sup> This cooling involves the collision of a carrier with a defect and an acoustic phonon. An additional cooling pathway has been shown to increase the rate of initial carrier cooling in graphene, with the carrier cooling rate reported to have a linear dependence on defect density.<sup>27</sup> The similitude of C-OP scattering rates for G3 and AG3 thus suggest that the lattice defect density in both samples is similar.

The 500 fs to 1 ps time range is marked by a persisting negative signal for all samples, as shown in the insets of Figure 5. The negative signal present across the full probe spectral range (440 – 680 nm) corresponds to excited state absorption. Similar persisting ( $\gg 1$  ps) negative  $\Delta T/T$  signal

for graphene films deposited on quartz has been previously reported.<sup>14</sup> The similar carrier dynamics and transient spectral features of ink-jet printed graphene ink (this work) with that of CVD grown graphene, both deposited on quartz, suggests that the carrier dynamics are independent of the preparation technique. Negative  $\Delta T/T$  signal could be ascribed to shrinkage of the band separation (band gap renormalization), driven by the photogenerated hot carriers, which in turn, are heating the lattice. Such dynamic behavior has been observed both in graphene<sup>15,24</sup> and graphite samples.<sup>25</sup>

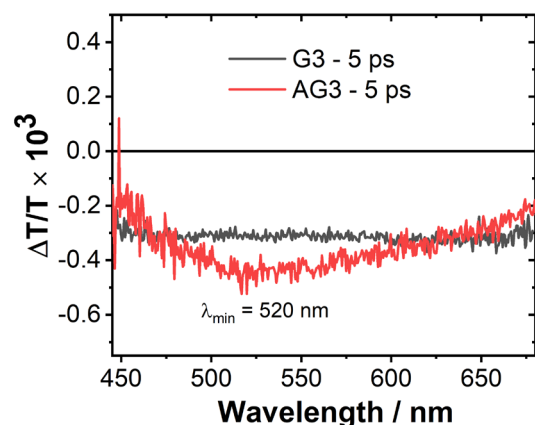


**Figure 6.** Kinetic traces at 550 nm for G3 and AG3. Inset corresponds to the expanded traces showing the negative recovery. The overlaid traces are the multiexponential fits, with the corresponding lifetimes (in ps) given in the legend. <sup>a</sup>Modeling the growth of the negative signal, not the recovery of the long-lived negative signal.

Negative  $\Delta T/T$  signals, when probing with near-IR photon energies (1.5 – 2.6  $\mu\text{m}$ ), have also been attributed to a rise of the Fermi level in doped graphene layers.<sup>6</sup> However, while probing in the UV-Vis range, we do not expect to monitor such small variations of Fermi level. The kinetic behavior of the negative transmission signal, at 550 nm, is shown in Figure 6, for G3 and AG3. In the case of G3, the maximum negative signal is reached at  $\sim 770 \text{ fs}$ , after which it decays biexponentially with lifetimes of 6.1 ( $\tau_1$ ) and 64 ps ( $\tau_2$ ). The decay component  $\tau_2$  is very similar to

the previously monitored monoexponential recovery reported by Shang.<sup>14</sup> As will be discussed subsequently, the relative contributions of  $\tau_1$  and  $\tau_2$  to the recovery of the negative signal seems to be power dependent and are both assigned to charge recombination and lattice cooling. In comparison to G3, the maximum negative signal for AG3 is reached at a pump-probe delay of 5 ps. The delay in reaching the maximum negative signal is reflected in the extraction of an additional lifetime of 0.9 ps, while fitting the growth of the negative  $\Delta T/T$  signal. Clearly, the incorporation of oxygen into the graphene structure and/or the more complex 3-dimensional structure of AG3 have a significant effect on the initial carrier dynamics. In AG3, about half of the negative signal decays with a lifetime of 51 ps, while the other half is non-decaying within the 400 ps time window of the experiment. Similar long-lived ( $\gg 1$  ns) negative  $\Delta T/T$  signal has been previously reported in graphene oxide suspended in water.<sup>28</sup> This signal was assigned by Kaniyankandy et al. to the presence of trapped states undergoing slow recombination. Via carrier quenching, the latter confirmed that the defect states mainly originated from oxygen sites, in the form of epoxides and carboxylic acid groups, which act as electron traps. The presence of similar kinetic behavior suggests the possibility of similar trapped states in AG3, which are not present in G3. Therefore, the 0.9 ps lifetime may be indicative of ‘trapping’ of the carriers by the oxygen sites. As previously alluded to, the AG inks also differ in flake morphology compared to the graphene inks, with the AG inks containing graphene flakes with a quasi-3D structure. The change in morphology cannot be discounted as a possible cause for the change in carrier dynamics observed. However, the AG films do not exhibit UV-Vis transmission spectra that are typical of 3D nanostructured graphene materials such as nanotubes.<sup>29</sup> This suggests that the 3D-flakes have optical transmission properties more akin to that of planar graphene sheets. Although the recovery dynamics of graphene oxide and AG3 exhibit similarities, the late-time transmission spectra do

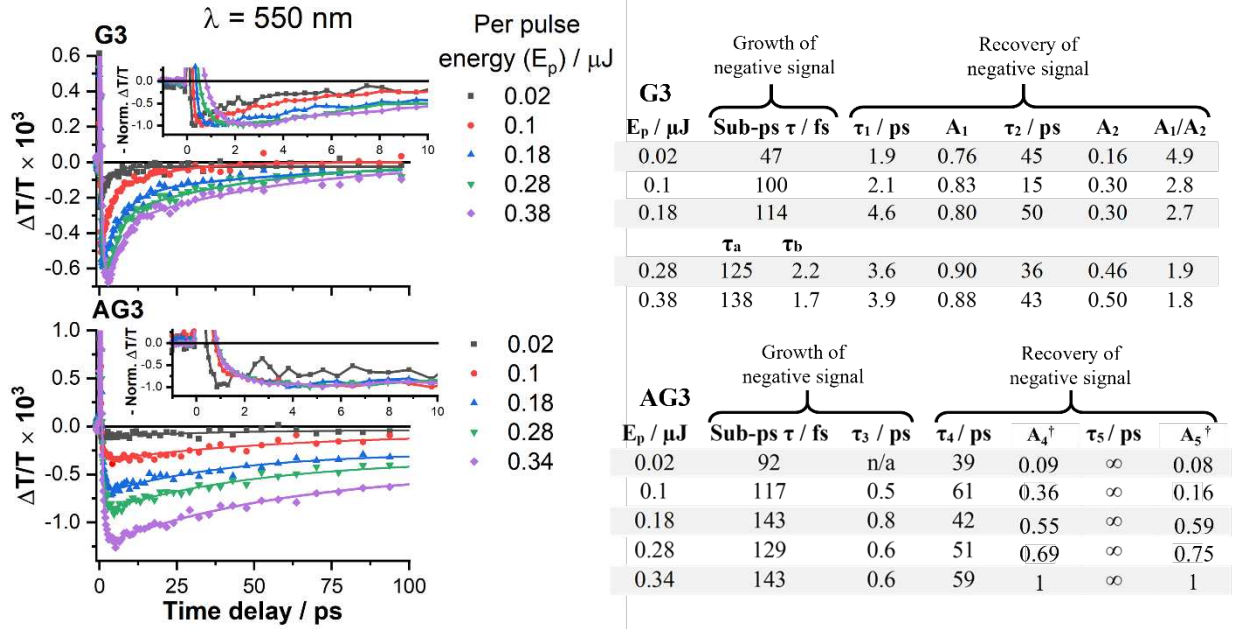
not. It has been reported that the absorption of trapped carriers (at oxygen sites) in graphene oxide has a peak at 670 nm.<sup>28</sup> AG3 displays no such peak at later time delays. However, there is a distinct peak at approximately 520 nm in AG3's transient transmission spectrum. This contrasts with G3, where the later time-delay spectrum is flat in the region 440 – 680 nm, as shown in Figure 7. This behavior suggests that the nature of electronic states responsible for the negative signal at late times are different in G3 and AG3.



**Figure 7.** The  $\Delta T/T$  spectra of G3 and AG3 5 ps after excitation at 400 nm. The minimum of the spectrum for AG3 is labelled on the graph.

Pump energy ( $E_p$ ) dependence of the kinetics at a probe wavelength of 550 nm are shown in Figure 8 for G3 and AG3. Multiexponential fittings reveal that the ultrafast, sub-ps, lifetime increases as  $E_p$  is increased, although the trend for the sub-ps lifetime of AG3 is weaker (see the ‘sub-ps lifetime’ columns in the tables given in Figure 8). This results in the maximum negative signal being reached at later pump-probe time delays for G3, as  $E_p$  is increased (see the inset in top left graph of Figure 8). For G3, the growth of the negative signal is monoexponential for  $E_p = 0.02, 0.1, 0.18 \mu\text{J}$ , whereas this growth is best fit with two exponential functions ( $\tau_a$  and  $\tau_b$ ) for  $E_p = 0.28, 0.38 \mu\text{J}$ . This signal dependence indicates that the nature of the initial carrier relaxation mechanism changes as  $E_p$  increases. A possible explanation for this behavior is the

presence of a hot optical phonon bottleneck at higher pump energies. Following excitation, the hot carriers will lose most of their energy to the formation of hot optical phonons via sequential C-OP scattering events.<sup>23</sup> The main optical phonon modes responsible for the energy dissipation are the intravalley ( $\Gamma$ ) and intervalley (K) optical phonons,  $K-A'_1$ ,  $\Gamma-E_{2g,LO}$  and  $\Gamma-E_{2g,TO}$ , where LO and TO are longitudinal and transverse optical phonons, respectively.<sup>22</sup>



**Figure 8.** (left) Pump energy dependent kinetics at 550 nm for both G3 (top) and AG3 (bottom). Five different energies are shown, ranging from 0.02 to 0.38  $\mu$ J, with the specific values given in the legend. (right) Table showing the lifetimes obtained from multiexponential fittings of the kinetics traces.  $^\dagger$ Amplitudes normalized to the maximum amplitude.

Subsequent cooling of the carriers is then coupled to the cooling of the hot optical phonons and as such,  $\tau_b$  may reflect the cooling rate of the hot optical phonons. At lower values of  $E_p$ , and therefore at lower carrier densities, it is possible that the role of a hot phonon bottleneck on the carrier relaxation dynamics is negligible. Conversely, the pump-probe time delay at which the maximum

negative signal is reached in AG3 seems independent of  $E_p$  (except for the 0.02  $\mu\text{J}$  trace, which is deemed unreliable due to the very low S/N level). We do not observe any obvious trend in the G3 recovery lifetimes  $\tau_1$  and  $\tau_2$ , as  $E_p$  is increased. However, the ratio of the  $\tau_1$  and  $\tau_2$  preexponential factors (amplitude  $A_1$  and  $A_2$ , respectively) steadily decreases from 4.9 to 1.8, when  $E_p$  increases from 0.02 to 0.38  $\mu\text{J}$ . With regards to AG3, the recovery kinetics ( $\tau_4$  and  $\tau_5$ ) also appear to be independent of  $E_p$ . If, as it is expected, the slowly recombining trapped carriers are responsible for the negative signal at late-time ( $> 400$  ps), then the signal is also expected to saturate at higher values of  $E_p$ . However, no saturation is observed, with the amplitude of the non-decaying signal increasing linearly with  $E_p$  (see the  $A_5$  column given of the table given in Figure 8). It is possible that the maximum pump energy reached in these experiments was insufficient to observe such behavior.

#### 4. CONCLUSION

The carrier relaxation dynamics of inkjet printed graphene and aerosol gel graphene films were investigated by means of ultrafast UV-Vis pump-probe spectroscopy. Similar ultrafast C-OP scattering lifetimes were observed for G3 (74 – 136 fs) and AG3 (110 – 126 fs), indicating that the lattice defect density in the novel aerosol gel ink is comparable to that of pure graphene ink. The C-OP scattering rates of the G and AG films showed a linear dependence on probe photon energy. Following the ultrafast C-OP scattering, the G films display a negative  $\Delta T/T$  signal, which recovers biexponentially (For G3,  $\tau_1 = 6.1$  and  $\tau_2 = 64$  ps at  $\lambda = 550$  nm). The kinetic recovery is assigned to recombination of carriers and the subsequent cooling of the lattice. Renormalization of the band gap is not excluded as a cause for the negative  $\Delta T/T$  signal, but further analysis is needed to disentangle the different contributions. In comparison to graphene films excited at energies  $<$

0.2  $\mu\text{J}$ , an additional lifetime was required to model the growth of the negative signal in the AG films. An additional lifetime of  $\sim 0.9$  ps was extracted from the multiexponential fitting of the AG3 kinetics. This additional kinetic component is assigned to trapping of the carriers, most probably due to the presence of oxygen in the AG films. Partial recovery of the negative  $\Delta T/T$  signal in the AG films is observed, resulting in a non-decaying signal, which can be attributed to the slow recombination of trapped carriers, in the  $> 1$  ns time scale. The similitude in the transient signals of AG and previously reported for graphene oxide points to the fact that the oxygen plays a major role in determining the carrier dynamics. Similarly, modelling of the ground state absorption spectra of our samples also points to the fact that oxygen is the main contributing factor. But we cannot exclude the possibility that AG's unique morphology also contributes to both, the non-decaying signal, and to the broadened steady state spectral features. To unambiguously differentiate the different roles played by the presence of oxygen and the unique morphology of AG films, we propose to investigate AG films with varying oxygen content. Such work is underway.

#### ASSOCIATED CONTENT

**Supporting Information.** Transient change in transmission spectra of the 1 pass and 2 pass graphene and aerosol gel graphene films. The corresponding kinetics, at select wavelength, for the aforementioned samples can also be found in the supporting information.

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# TOC graphic

