

# Self-Healing Reduced Graphene Oxide Films by Supersonic Kinetic Spraying

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The industrial scale application of graphene and other functional materials in the field of electronics has been limited by inherent defects, and the lack of simple deposition methods. A simple spray deposition method is developed that uses a supersonic air jet for a commercially available reduced graphene oxide (r-GO) suspension. The r-GO flakes are used as received, which are pre-annealed and pre-hydrazine-treated, and do not undergo any post-treatment. A part of the considerable kinetic energy of the r-GO flakes entrained by the supersonic jet is used in stretching the flakes upon impact with the substrate. The resulting “frozen elastic strains” heal the defects (topological defects, namely Stone-Wales defect and C<sub>2</sub> vacancies) in the r-GO flakes, which is reflected in the reduced ratio of the intensities of the D and G bands in the deposited film. The defects can also be regenerated by annealing.

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## 1. Introduction

The high thermal conductivity, excellent electrical mobility, and superior mechanical stiffness and fracture strength<sup>[1–5]</sup> of graphene has attracted the attention of a broad spectrum of scientists and engineers. Graphene is particularly attractive for applications such as optoelectronics, which require materials possessing superior chemical stability, ballistic electron transport, and high optical transmittance.<sup>[6,7]</sup>

However, there are still many challenges facing the introduction of graphene into mainstream nanoelectronics. For example, there are currently no economically viable low-cost and large-scale production methods that preserve the original properties of graphene.<sup>[8]</sup> There are a few

graphene deposition methods; foremost among them being the well-known mechanical exfoliation/cleavage of graphite, also known as Scotch-tape-peeling, which produces high-quality graphene sheets.<sup>[1,7]</sup> Although popular, this method is not scalable for large-scale production. One of the most promising methods for producing high-quality graphene films is chemical vapor deposition (CVD). Kim et al.<sup>[9]</sup> showed that the transparency and electrical conductivity of CVD-grown graphene films were as high as those of the mechanically cleaved films; however, the use of CVD for large-scale production is limited by a number of factors. First, CVD requires high temperatures (in excess of 900 °C),<sup>[10]</sup> which precludes the use of flexible polymer substrates. Second, it requires pre-patterning of the catalyst<sup>[11]</sup> and single-crystal substrates,<sup>[8]</sup> which in turn requires the transfer of the grown film, thereby increases the number of processing steps. Third, the growth of a graphene film by CVD on a single rigid Ni substrate requires etching, the time requirement of which increases exponentially with the size of the film.<sup>[12]</sup> Fourth, the inhomogeneous reaction temperature inside a CVD furnace hinders the large-scale production of uniform graphene films. Finally, currently there is no industrially scalable method for creating an energy gap at the K and K' points in the Brillouin zone, which is required for the utilization of graphene in industrially viable technology. The few methods that have been explored in an attempt to tune the energy gap include the formation of graphene quantum dots,<sup>[7]</sup> patterning of

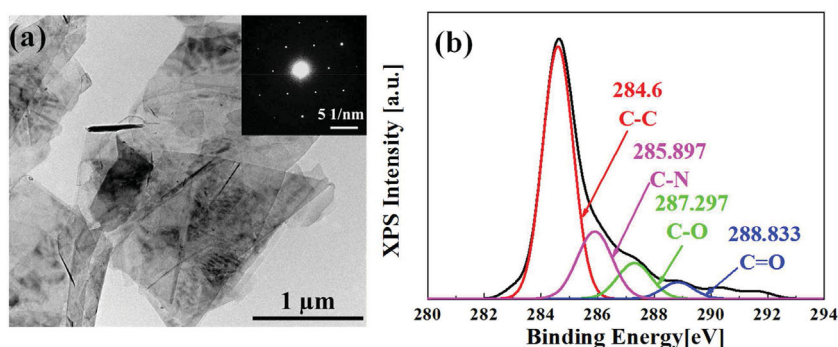
graphene on nanoribbons,<sup>[13]</sup> and stretching of deposited graphene.<sup>[14]</sup> For large scale application, industrially scalable mechanical and/or chemical exfoliation seems to be the only possible path. However, the method is prone to produce defective graphene. It should be emphasized that the defects significantly affect the physicochemical properties of graphene. The problem is more pronounced for r-GO, which is one of the most promising avenues for large-scale graphene deposition. As an example, a highly oriented graphene would have an electrical conductivity, which is two order of magnitude higher than that of r-GO.<sup>[15,16]</sup> To eliminate these defects, several methods were explored: e.g., chemical treatment,<sup>[17]</sup> plasma treatment,<sup>[18]</sup> annealing<sup>[19]</sup> etc. However, these methods require an expensive post-treatment of r-GOs.

There are numerous solution-based deposition methods that are currently available.<sup>[20]</sup> Dispersed GO has generally been deposited by spray coating,<sup>[6,21]</sup> dip coating,<sup>[22]</sup> spin coating,<sup>[8,23–26]</sup> and inkjet printing.<sup>[27]</sup> Among these methods, spray coating offers the unique advantages of allowing control over solvent evaporation, preventing aggregation of the GO sheets, and producing films of uniform thickness.<sup>[6]</sup>

In the present work, we developed a unique kinetic spray deposition scheme that exploits the supersonic acceleration of droplets through a converging/diverging de Laval nozzle.<sup>[28]</sup> The reduced graphene oxide (r-GO) precursor (an aqueous suspension of GO flakes) was injected by air drag into the nozzle throat, wherein the precursor was atomized upon exposure to the high-speed gas stream. The advantage of the kinetic spray method is that it produces very small droplets through supersonic shearing of the injected r-GO precursor. The shear instability, together with the high-speed flow, promotes the uniform dispersion of droplets seeded by the GO flakes. The droplets evaporate rapidly, reducing the tendency for r-GO flakes to concentrate<sup>[6]</sup> and aggregate.<sup>[29]</sup> The enormous energy supplied by the supersonic jet results in stretching of the graphene and subsequent healing of defects, a phenomenon unique to this method and not observed for any of the other previously studied methods. Experiments conducted using kinetic spraying of GO flake suspensions, and the subsequent results, are described and discussed below.

## 2. Results and Discussions

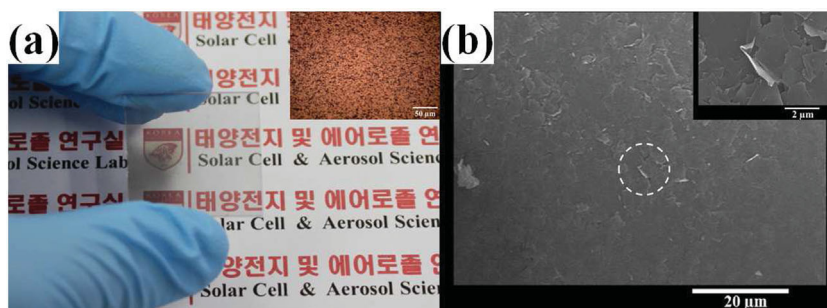
Figure 1a shows a transmission electron microscope (TEM) image of the exfoliated r-GO flakes used to prepare the r-GO suspension. The flakes are comprised of a few r-GO sheets (or atomic layers), with no other carbon-related nanostructure found. The inset in Figure 1a shows the electron diffraction (SAED) pattern of the r-GO flakes within the selected area shown in the TEM



**Figure 1.** (a) TEM image of typical r-GO flakes. The individual flakes extend a few micrometers in length and demonstrate a quite wrinkled surface morphology. The inset shows the SAED pattern, which indicates that each graphene flake consists of a small number of individual graphene sheets. (b) XPS of the r-GO flakes used to prepare dispersions.

image. The SAED pattern confirms the crystallinity of the r-GO flakes and their symmetrical hexagonal structure. From the SAED we determined the lattice constant to be  $2.35 \pm 0.12$  Å, which is consistent with that of a previous study.<sup>[33]</sup> X-ray photoelectron spectroscopy (XPS) was also used to analyze the chemical state of the surface of the r-GO film deposited on the substrate (Figure 1b). The de-convoluted XPS spectra of the r-GO films showed that the XPS spectra can be fitted by four peaks with binding energies of 284.6, 285.897, 287.297, and 288.833 eV; which corresponded to C–C, C–N, C–O, and C=C chemical bonds, respectively. The C–C, C–O, and C=C bonds were produced by the r-GO flakes. The C–N bond on the other hand was due to the use of hydrazine as the reducing agent, with nitrogen likely forming a covalent bond with the surface of the r-GO film during the reduction process. These observations clarify the chemical and structural composition of the materials of the present work, and reveal no anomalous behavior.

Representative images of the r-GO film deposited by kinetic spraying on transparent soda lime glass at room temperature are shown in Figure 2. It should be mentioned that the r-GO film was not post-treated in any way. It can be seen from Figure 2a that the glass on which the r-GO film was deposited appeared light grey in color. The color and transparency of the



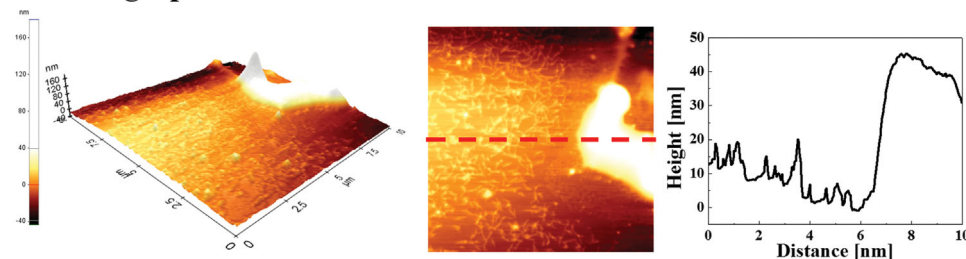
**Figure 2.** (a) Kinetic-spray-deposited r-GO film on soda-lime glass (10 wt% of r-GO flakes suspended in ethanol). The graphene film transmittance was 72.7% for  $\lambda = 550$  nm and the sheet resistance was  $19 \text{ k}\Omega/\text{sq}$ . The corresponding optical microscope image is shown in the inset. Panel (b) shows a SEM image of the deposited r-GO film; the inset is a zoomed-out image of the area encompassed by the dashed circle in the main image.

glass are expected to change with increasing the concentration of r-GO flakes in the suspension, and with the thickness of the deposited film. The deposition method is highly controllable because the thickness of the deposited r-GO film can be easily varied by altering either the concentration of the precursor suspension, or the deposition time. It also needs to be mentioned that the film thus deposited was very thin ( $\sim 10$  nm), which also attests to the fact that given the processing conditions, the existence of any residual solvent is absolutely improbable. The area covered by the spray can also be increased by simply sweeping the nozzle over a larger substrate area. The optical image in the inset of Figure 2a shows that on a macroscopic scale the r-GO flakes were relatively uniformly mixed and evenly distributed over the entire surface of the substrate. No visible agglomeration of the flakes was apparent, which indicates sufficient uniformity of the r-GO film. The scanning electron microscope (SEM) image of the deposited film in Figure 2b shows that the r-GO flakes were well distributed and uniformly covered the entire substrate when sprayed with r-GO suspension diluted to 10 wt% solution. The magnified view in the inset of Figure 2b shows that there were some surface undulations present. A detailed surface topography was subsequently measured by AFM (Figure 3) for all the suspensions. The AFM images in Figure 3 show spray-coated samples for different concentrations of r-GO flakes in the precursor suspension. It can be seen

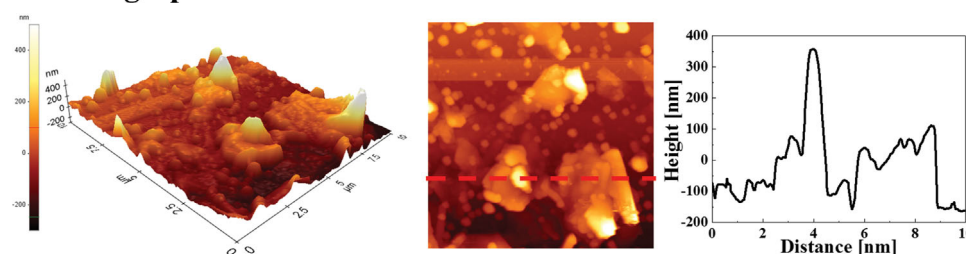
from these images that the roughness of the deposited film for the 10 wt% r-GO suspension had a variance of  $\pm 10$  nm. From the 3D image in Figure 3, it can be seen that while spraying 10 wt% r-GO suspension the area of the deposited film was relatively smooth, for 25 and 33.3 wt% r-GO suspensions the surface was rougher with a variance of about 100 nm. This can be explained by the fact that the incoming air stream atomizes the r-GO suspension, with a finer atomization leading to a smoother coating. A higher concentration of r-GO flakes in the suspension increases the effective viscosity, which consequently results in poor atomization. The resulting roughness of the deposited film diminishes its transmittance, as illustrated in Figure 4.

Figure 4a–c shows the three spray-coated glass slides on which 10, 25, and 33 wt% r-GO flake suspensions were deposited. Figure 4d quantifies how increasing the r-GO concentration in the suspension from 10 to 33 wt% reduced the transmittance from 70% to 30%. In addition, Figure 4d also shows that the transmittance was constant for wavelength  $\lambda$  values above 400 nm, which is suitable for solar cells, displays, and optical communication.<sup>[24]</sup> Figure 4e shows the correlation between the resistance and transmittance of the deposited film.<sup>[8,29,34–38]</sup> Figure 4f shows that light-emitting diodes (LEDs) continued to glow when the r-GO coated substrate was manually bent, which clearly demonstrates that the conductive path of the deposited

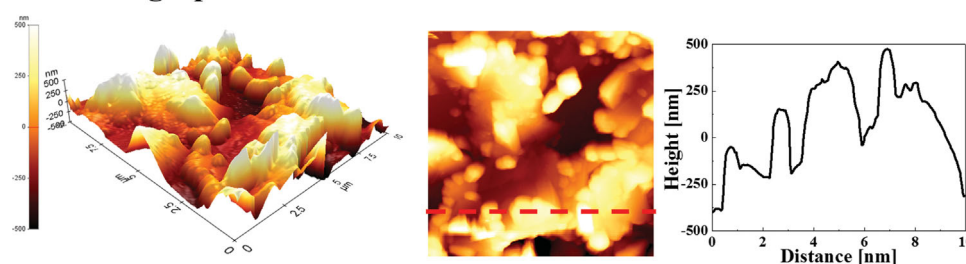
### 10 wt% graphene



### 25 wt% graphene

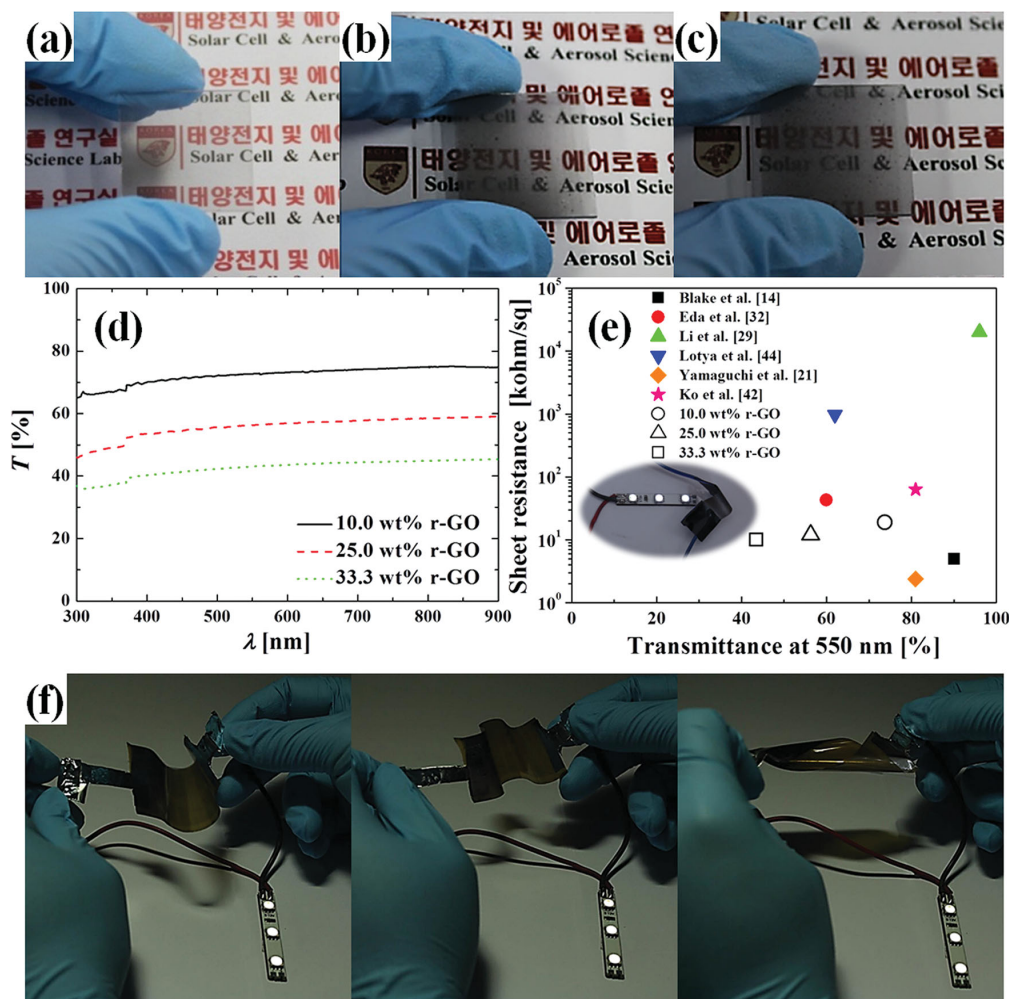


### 33.3 wt% graphene



**Figure 3.** AFM images of the r-GO films showing typical r-GO flakes; (left) 3D and (middle) 2D views. The surface roughness of the path indicated by the dashed red lines in the 2D views is illustrated by the curves on the right.





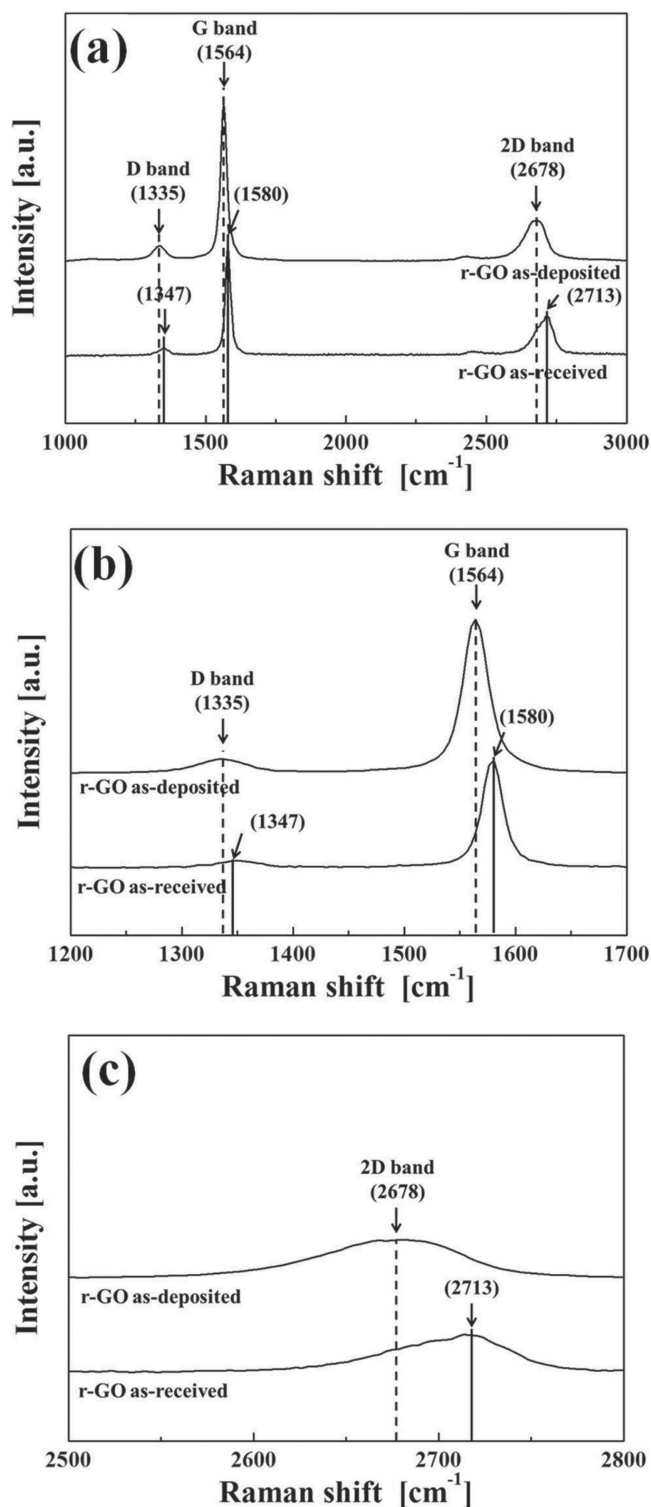
**Figure 4.** Evaluation of visual transmittance for the three films deposited from (a) 10 wt%, (b) 25 wt%, and (c) 33 wt% dispersions. (d) Transmittance  $T$  versus wavelength. (e) Comparison of the present results with those reported in the literature. (f) Flashing of LEDs included in a circuit passing a r-GO-coated flexible substrate subjected to bending: light remains on irrespective of the degree of bending.

film was not broken. This was an exhibition of the robustness of the r-GO films deposited by our proposed method. **Table 1** compares our resistance and transmittance results with those of other researchers who used other deposition methods. It can be seen that although our transmittance values are comparable with those of previous studies, our sheet resistance values are

typically lower, with the exception of the two cases noted with the diamond and filled-square symbols in Figure 4e. It should be noted that our deposition method is simpler than those that produced the other results seen in Table 1. More importantly, it is also industrially scalable with a 10 wt% r-GO flake suspension preferred due to its superior performance. This industrial

**Table 1.** Comparison of transparency and conductivity of the r-GO films deposited by different processes.

| Reference      | Sheet resistance [k $\Omega$ /sq] | Transmittance [%] | Substrate                          | Coating method/process                                                                                                                      |
|----------------|-----------------------------------|-------------------|------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------|
| Ref. [34]      | 5                                 | 90                | glass                              | solution spin and spray coating                                                                                                             |
| Ref. [36]      | 43–100                            | 60–98             | membrane, glass, plastic substrate | GO suspension was filtered and the deposited GO film was reduced with dimethylhydrazine vapor and annealed at 200 °C in nitrogen atmosphere |
| Ref. [35]      | 20,000                            | 96                | membrane                           | Reduced GO with hydrazine in aqueous basic condition and then spray-coated                                                                  |
| Ref. [47]      | 970                               | 62                | membrane                           | Vacuum filtration                                                                                                                           |
| Ref. [8]       | 0.6–2.4                           | 40–81             | membrane                           | spin coating method                                                                                                                         |
| Ref. [29]      | 62.8                              | 81                | PET, glass                         | doctor blade                                                                                                                                |
| Present result | 10–19                             | 43.5–73.7         | glass                              | Solution precursor cold spray                                                                                                               |



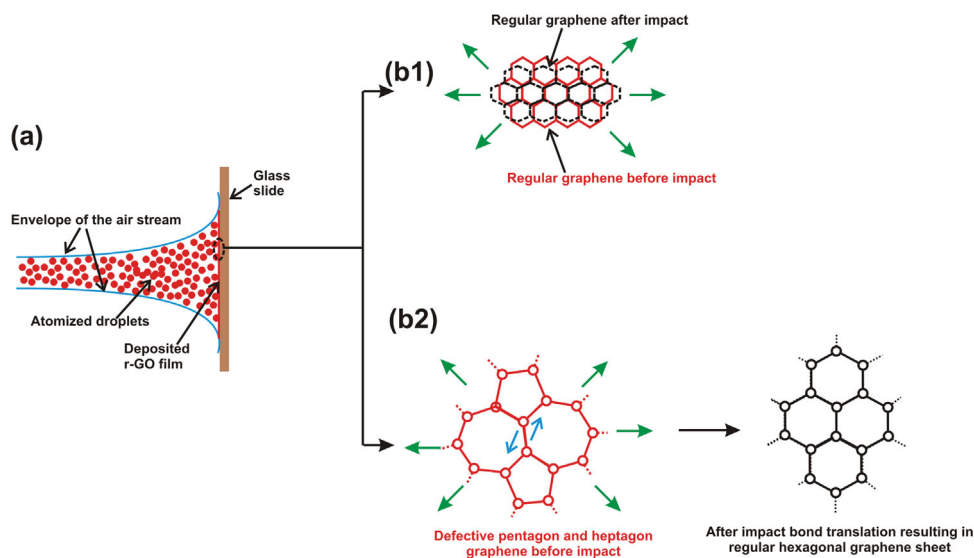
**Figure 5.** (a) Raman spectra of the precursor r-GO flakes and the deposited r-GO film. (b) Zoomed-in view focusing on the D and G band. (c) Zoomed-in view focusing on the 2D band.

scalability, along with the ability to control surface roughness to within  $\pm 10$  nm, makes our process unique and is only made possible because of the supersonic air jet used. Note also that

Raman spectroscopy is a non-destructive method, and does not induce any defects or damage within the sample like the electron beam of a TEM (in addition, TEM cannot be used because the deposited r-GO flakes are multi-layered).

For complete characterization of the deposited r-GO films, Raman spectroscopy of the deposited r-GO flakes was conducted and the results compared with those for the original r-GO flakes (before deposition). Figure 5a shows the overall comparison, whereas Figure 5b, c shows magnified views close to the G, D band and 2D band, respectively. During the Raman spectroscopy of the r-GO film, the following important peaks were observed: the D peak ( $\sim 1350$   $\text{cm}^{-1}$ ), the G peak ( $\sim 1580$   $\text{cm}^{-1}$ ), and the G' or 2D peak ( $\sim 2700$   $\text{cm}^{-1}$ ).<sup>[39]</sup> In the Raman spectra of r-GO the D peak originates from a defect due to the inter-valley scattering. The G peak is associated with the double-degenerate  $E_{2g}$  mode, whereas the 2D peak was due to the second-order zone boundary phonons. In addition, the D peaks were due to the presence of defects.<sup>[39]</sup> The Raman spectroscopy results in Figure 5 show that in the present case there were differences in the positions of these characteristic peaks between the original and deposited r-GO flakes. It can be seen that after impact the 2D peak of the deposited r-GO film was shifted by  $-35$   $\text{cm}^{-1}$  (Figure 5c), whereas the G peak was shifted by  $-16$   $\text{cm}^{-1}$  (Figure 5b) from that of the as received r-GO before impact. This could only have happened if the carbon-carbon bond had been irreversibly elongated (i.e., irreversibly strained), as was observed in a previous study.<sup>[14]</sup> The irreversible strain generation can be explained as a result of the supersonic jet atomizing the r-GO suspension into droplets of size:  $a = \sigma/(\rho_a U^2)$ , where  $\sigma$  is the surface tension of the solvent,  $\rho_a$  is the air density, and  $U$  is the blowing velocity. For  $U = 400$  m/s the droplet size was about 1  $\mu\text{m}$ , which means that each droplet contained approximately the same number of a few r-GO flakes. On the other hand, this size is of the same order as the smallest eddies in the gas jet (the Kolmogorov eddies), and no further stretching or fracture of the r-GO flakes was therefore expected. The droplets were fully entrained by the gas flow, the solvent evaporated almost immediately, and the r-GO flakes impacted the substrate at a velocity of the order of  $U$ . The specific energy associated with the impact is of the order of  $E_k = (\rho U^2)/2$ , where  $\rho$  is the density of the r-GO flake. This energy was converted into the elastic energy of the flake as it was radially squeezed and stretched by the impact. The specific elastic energy is given by  $E_e = E\varepsilon^2/2$ , where  $E$  is the Young's modulus ( $\sim 1$  TPa for a single r-GO flake), and  $\varepsilon$  is the strain. Neglecting losses, it can be assumed that  $E_k = E_e$ ; hence,  $\varepsilon$  is  $\sim 1.7\%$ . Such strains of r-GO can already be sufficient for irreversible plastic deformations, which can be "frozen" in the graphene flakes after the impact. According to Ni et al.,<sup>[14]</sup> the shift in the 2D band Raman frequency for a single r-GO layer is  $-27.1$  and  $-21.9$   $\text{cm}^{-1}/\%$  for three-layered r-GO; and the shifts for the G bands are  $-14.2$  and  $-12.6$   $\text{cm}^{-1}/\%$ , respectively. As a result, this irreversible straining of 1.7% could create a shift in the Raman peaks.<sup>[14]</sup> Figure 6b(1) is a schematic illustration of the impact stretching of regular hexagonal r-GO sheets.

It should be emphasized that the higher the ratio of the intensity of the D peak to the intensity of the G peak, the higher is the number of defects. The low ratio of the intensity

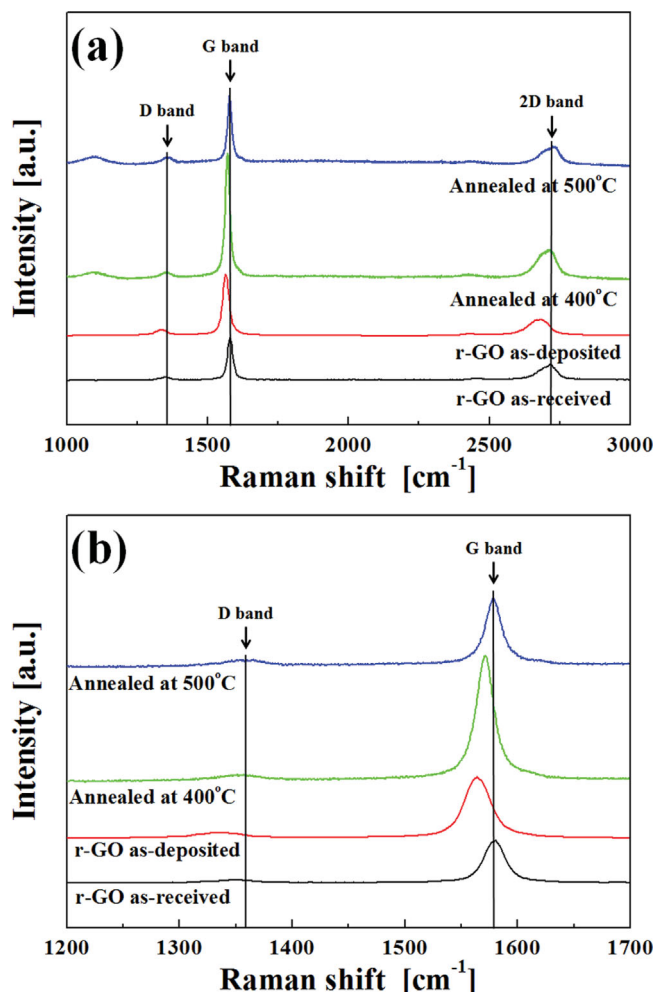


**Figure 6.** Schematic of the (a) deposition of r-GO onto a glass slide, and (b1–2) stretching of regular, and pentagonal and hexagonal r-GO sheets caused by impact. Panel (b2) shows that stretching of pentagonal and heptagonal r-GO sheets results in bond translation along the direction of the blue arrows, resulting in healing of r-GO sheets by impact onto a substrate.

of the D peak to that of the G peak shows that our deposition method did not add new defects to those already present in the parent r-GO flakes. Indeed, the intensity ratio of the original r-GO flakes in suspension was  $I(D)/I(G) = 0.62$ , whereas that of the deposited film was even lower, namely 0.22. This indicates that the number of defects in the deposited films was lower than that in the original r-GO flakes and this implies that r-GO flakes were healed during deposition. It has been shown that in the presence of the excess carbon atoms, healing of small defects in graphene occurs spontaneously without energy supply,<sup>[40]</sup> and that a metallic support plays a crucial role in the healing of Stone-Wales defects.<sup>[41]</sup> In our case, we used r-GO flakes containing small defects and supplied a significant amount of energy ( $E_k$ ) from the supersonic air jet. Our results show that these conditions facilitate a rapid healing of defects through stretching of the r-GO flakes during the deposition process. For comparison, much higher values for the  $I(D)/I(G)$  ratio in the range of 1.26 – 1.6 have been previously reported by others.<sup>[21]</sup> Our lower  $I(D)/I(G)$  ratio indicates that the atomic carbon structure of the r-GO films produced by our deposition method had a lower defect level than previously achieved in Refs. [42,43]. There can be two types of topological defects present in the system: Stone-Wales defect [5–7–7–5 ring structure] and  $C_2$  vacancies; 5–8–5 ring structure.<sup>[44]</sup> In Ref. [44], the Raman peaks associated with these topological defects were clearly elucidated. Similar to Ref. [44], in the present scenario the absence of defects above  $1650\text{ cm}^{-1}$  can be explained by the fact that concentration of such defects in the samples is very low. It can also be seen from Ref. [44] that the Raman peaks corresponding to both types of topological defects are almost superimposed, which makes it difficult to differentiate these two types of defects. The healing of defects by stretching can be illustrated using the schematic in Figure 6b(2). For the sake of simplicity, only healing of the Stone-Wales defects is shown here. The stretching of the seven- and five-membered rings draws them closer, which results in the bridging of the defects.

As shown in Figure 6b(2), the impact caused bond translation and the formation of a regular hexagonal sheet, the stretching of which continued even after the impact. This indicates that the healing of the topological defects in r-GO occurred within 0.2 ms, which is around the characteristic time of 1 ms of our deposition method evaluated above. On the other hand, the healing of holes in r-GO is highly improbable, as the process occurs over a time frame of 10 s and requires a supply of excess carbon.<sup>[40]</sup> Moreover, as noted earlier the healed defects were regenerated by annealing, which is also indicative of topological defects. Besides, it was also shown in Ref. [44] that the existence of these topological defects result in curvature of the r-GO flakes. A strong impact and stretching also facilitates removal of the curvature resulting in healing of the defects. It needs to be mentioned that although it is very tempting to rely solely on visual observation of defects by TEM, it should be borne in mind that such observations are only possible for monolayer sheets. To avoid defect generation through handling or preparation of a sample for observation by TEM, the sample should be collected during deposition. This was attempted several times in the present work but unfortunately the deposited samples were always found to be multilayered, thus precluding any chance of direct observation similar to that used by other researchers.<sup>[40,41]</sup> One such image is shown in the supplementary section (cf. Figure S1). The only possible way to observe a monolayer of the as deposited r-GO flakes was to exfoliate the multilayer by sonication (cf. Figure S2). However, due to the sonication, it was almost impossible to establish unequivocally the origin of these defects. Moreover, it is emphasized that mere observation of monolayer r-GO sheets can also result in defects caused by the oncoming electron beam, unless conducted under specialized experimental conditions.<sup>[1]</sup> For distinguishing defects, the most reliable non-destructive method is therefore Raman spectroscopy,<sup>[39,45]</sup> as mentioned earlier.

It should be emphasized that it is a general practice to improve the quality of as-deposited r-GO flakes by heating



**Figure 7.** Comparison of the Raman spectra for deposited r-GO films before and after annealing at 400 °C and 500 °C, and before deposition. The inset lists the relative positions of the D, G and 2D bands, and the corresponding  $I(D)/I(G)$  ratios.

(annealing) or post-treatment by chemicals, but in our process the defects are healed by the energy supplied through the impact. Note that it is very tempting to conclude that the shift stems from multiple layers of deposited r-GO flakes. However, such a conclusion would be incorrect. Indeed, the Raman spectra of the as-received r-GO flakes clearly show the presence of a wide but well-defined peak at  $2713\text{ cm}^{-1}$ , which is similar to Refs [45,46]. In the latter works it was shown that owing to the existence of multiple monolayers, the 2D peak widens and remains around  $2700\text{ cm}^{-1}$ . Thus, the shift of the wide 2D peak after deposition cannot stem from multiple monolayers but rather is associated with the effect of impact.

To examine the effects of annealing on the as-deposited r-GO sheet deposited r-GO films were annealed at 400 °C and 500 °C in air, and then characterized by Raman spectroscopy. Figure 7 and Table 2 compare the Raman spectra obtained both before and after annealing (cf. Figure 5). It can be seen that after annealing, the peaks of the G, D, and 2D bands move to exactly the same positions as they were in the precursor dispersion. It can also be seen that the  $I(D)/I(G)$

**Table 2.** The comparison of Raman peaks of the original r-GO in suspension, the deposited r-GO, and deposited r-GO after annealing.

|                                | D band | G band | 2D band | $I(D)/I(G)$ |
|--------------------------------|--------|--------|---------|-------------|
| Original r-GO in suspension    | 1347   | 1580   | 2713    | 0.62        |
| Deposited r-GO (graphene film) | 1335   | 1564   | 2678    | 0.22        |
| Annealed at 400 °C             | 1353   | 1571   | 2715    | 0.56        |
| Annealed at 500 °C             | 1354   | 1578   | 2724    | 0.83        |

ratio increased to 0.56 after annealing at 400 °C, and to 0.83 after annealing at 500 °C. This means that annealing actually increased the defects in the system. A detailed characterization done using XPS is shown in supplementary information (cf. Figure S3 and Table A1) The XPS shows that defect generation can result from one of the two following reasons (either separately, or as a combination of both): (a) It has previously been shown<sup>[41]</sup> that the growth of graphene at 400–500 °C produces structural disorder and defects in the system. The annealing of graphene at high temperatures subsequently results in rotation and translation of the C—C bond. This clearly shows that the heating during the annealing process increased the energy beyond the activation energy barrier for the C—C bond rotation. Consequently, the “frozen elastic strains” were eased and the defects could regenerate. (b) Annealing can result in depletion of nitrogen and oxygen from the system, thus leading to a smaller  $\text{sp}^2$  domain and the generation of defects. A similar behavior was observed after annealing polyacrylonitrile, which resulted in the elimination of  $\text{CH}_2$  and CN groups.<sup>[47–49]</sup>

The existing methods of deposition for high quality (i.e. with few defects) r-GO<sup>[14]</sup> involve sophisticated handling that is not economically feasible on an industrial scale. To the best of our knowledge, the present work is the first to propose a robust and industrially scalable method for producing a self-healing r-GO film.

### 3. Conclusion

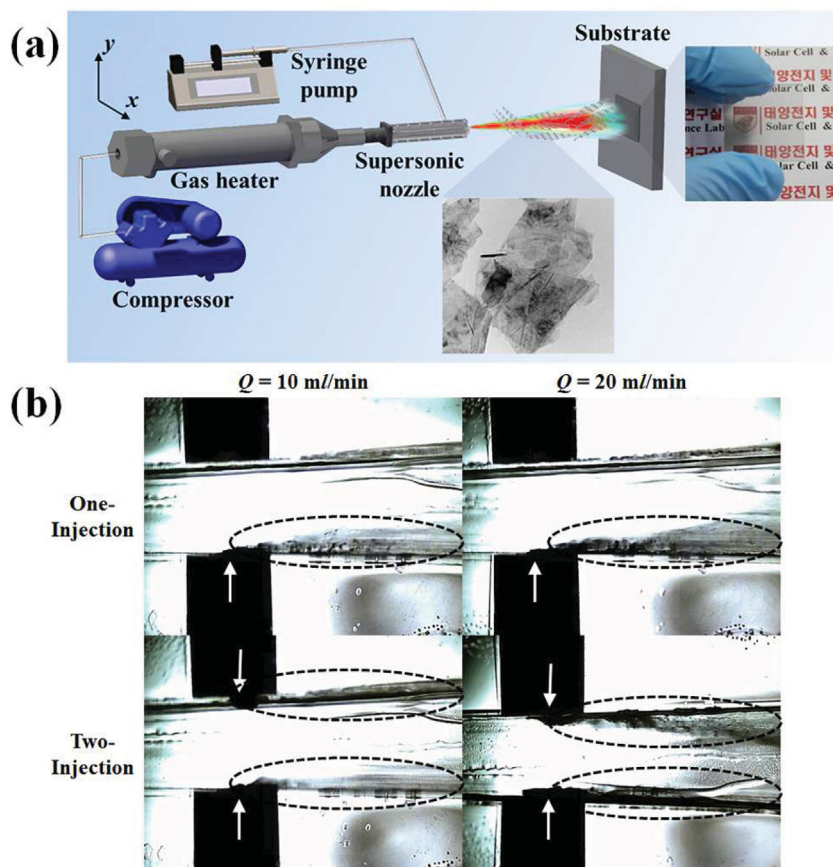
We report an industrially scalable method for depositing r-GO flakes by supersonic atomization and spraying. Unlike other methods, no post-treatment is required and the deposition can be performed on any substrate, including polymeric and flexible substrates. The deposition process led to significant irreversible straining of the r-GO flakes, resulting in the healing of the Stone-Wales defects. In contrast, subsequent annealing was shown to diminish the strains, and led to the defect regeneration.

## 4. Experimental Section

### 4.1. Preparation of Precursor Suspension

The hydrazine-treated r-GO solution consisting of r-GO flakes (product name: BM-GI from BMS Tech, Korea) dispersed in ethanol was purchased Besides ethanol, the solvent included toluene, methyl-ethyl ketone (MED), dimethylformamide (DMF), N-methylpyrrolidone (NMP), butyl-carbitol acetate (BCA), which were used as dispersants.





**Figure 8.** (a) A schematic of the kinetic spray system used to atomize and deposit the r-GO suspensions. (b) The atomization process as observed through the transparent acrylic nozzle (seen as a horizontally orientated wedge-like configuration). The acrylic nozzle sustains a supersonic gas flow in its widening part. The r-GO suspension is supplied through the black channel (oriented vertically) in the direction of the arrows. The suspension enters the gas flow in the supersonic part of the nozzle and is atomized by the gas cross-flow. The resulting multi-phase domains with gas-droplet flow are indicated by the dashed lines.

The as-received r-GO solution was too thick to spray. Thus pure ethanol was added to dilute the r-GO solution with the weight ratio of the r-GO solution to ethanol in the range of 10–33.3 wt%. The purpose of varying concentration of the r-GO solution was to modulate either the coating density or film thickness by changing spraying capability. Ethanol resulted in more efficient atomization and evaporation faster than water owing to its lower viscosity, surface tension, and higher volatility.

#### 4.2. Precursor Suspension Injection and Atomization

**Figure 8a** depicts a schematic of the experimental setup for the injection and atomization of the r-GO suspension; including the gas tank, syringe pump, stainless steel nozzle, and x-y stage used. This setup was also equipped with a transparent acrylic nozzle of identical dimensions to the stainless steel nozzle, which was used for visualization of the atomization process as shown in **Figure 8b**. Atomization results in droplets on the scale of  $a = \sigma/\rho_a U^2 = 10^{-4} - 10^{-3}$  cm, where  $\sigma$  is surface tension of liquid, and  $\rho_a$  and  $U$  are the air density and velocity.<sup>[30,31]</sup> According the  $a^2$ -law with the convective component, it takes about 1 ms for such droplets to evaporate.<sup>[30,32]</sup> This means that the suspension droplets fully evaporate over the distance of a few centimeters, and thus, r-GO flakes or their clusters impact onto the substrate being completely dry.

It should be emphasized that all quantitative data was acquired from the stainless steel nozzle, because the acrylic nozzle could not withstand the high temperature of the heated air. The nozzle dimensions are listed in **Table 3**. The temperature of the nozzle exit was kept at 350 °C. It is worthy to mention that this process is called kinetic spray because the temperature used here is lower than the melting point of the sprayed materials and the temperature is used to provide supersonic velocity of gas jet, where the supplied thermal energy is converted to kinetic energy.

The substrate was located 60 mm from the nozzle exit. The nozzle exit was installed on a maneuvering stage that traversed the 50 mm length of the substrate in about 4.17 s (i.e., the nozzle's passing/scanning speed was about 12 mm/s in both the x and y directions shown in **Figure 8a**). The moving nozzle could traverse the length of any fixed substrate that might be required for a larger coating area. The atomized r-GO suspension droplets moved through open air at room temperature until they were deposited on either the soda-lime glass or flexible polyimide substrates used to produce the r-GO films. All substrates were cleaned by an ultrasonic acetone bath for 10 min prior to use. Pressure injection by a syringe pump (KDS100) was used to supply the r-GO suspension at a flow rate of 10–20 mL/min. The r-GO suspension was injected into the de Laval nozzle near the throat as shown in **Figure 8b**, in which the first row snapshots correspond to a single injection from the bottom, and the second row snapshots correspond to two injections from the bottom and the top, respectively. A high-speed camera (Vision Research, Inc., Phantom 7.3) equipped with a zoom lens (1.56 mm/pixel) and Halogen lamp (250 W) was used to capture the atomization process inside the supersonic nozzle (**Figure 8b**). The injected r-GO suspension was exposed to significant aerodynamic forces in the supersonic cross-flow of the gas and was almost instantaneously atomized into tiny droplets. The size of the droplets could be controlled by changing the speed of the air cross-

flow; the greater the speed, the smaller the droplets that were created. The injection flow rate of the r-GO suspension also affected the droplet size, but it is important not to overload the gas flow with the suspension in order to avoid poor atomization. The atomized droplets were quickly entrained and accelerated in the de Laval nozzle by air drag. The nozzle air injection inlet pressure  $P_0$  was 6 bar and the pre-heat temperature  $T_0$  was 350 °C. The resultant air volumetric flow rate through the nozzle was around 1.57 m<sup>3</sup>/min. The accelerating droplets of the atomized suspension were also heated in the gas flow inside the nozzle, which resulted in rapid evaporation of the solvent and eventual deposition of

**Table 3.** The nozzle dimensions. ( $D_i$ : inner diameter,  $D_t$ : throat diameter,  $D_e$ : exit diameter,  $L_c$ : length of the converging section,  $L_d$ : length of the diverging section)

| Nozzle parameters | Values [mm] |
|-------------------|-------------|
| $D_i$             | 10          |
| $D_t$             | 6           |
| $D_e$             | 8.8         |
| $L_c$             | 40          |
| $L_d$             | 100         |



residual r-GO flakes on the substrate. It needs to be mentioned here that the boiling point of DMF is 153 °C and the boiling point of methanol 145 °C. Given the temperature at the nozzle exit and high velocity of surrounding air jet, it is absolutely improbable to have any residual of DMF and/or methanol. In addition to that after collection of the r-GO flakes, the coated substrates were characterized after collection for few days, which eliminated the chances of existence of any residual solvent.

### 4.3. Material Characterization

The surface microstructure of the deposited r-GO flakes was characterized using a high-resolution scanning electron microscope (SEM) (HRSEM, XL30SFE Phillips Co., Holland) operated at 10 kV, and a transmission electron microscope (TEM) (EM420, Philips Electron Optics, Eindhoven, The Netherlands). An atomic force microscope (AFM) (Xe-100, Park Systems) in noncontact mode was used to examine the surface morphology and roughness of the deposited r-GO films. Raman spectroscopy (Renishaw MicroRaman/Photoluminescence System) was used to analyze the crystal quality of the kinetically-sprayed films formed by the deposited r-GO flakes, and their structural imperfection. X-ray photoelectron spectroscopy (XPS) (PHI5600, Physical Electronics) was also used to analyze the elemental compositions and assign the carbon peaks.

### Supporting Information

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

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- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. Firsov, *Science* **2004**, *306*, 666.
- [2] Y. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, *Nature* **2005**, *438*, 201.
- [3] X. Wang, Y. Ouyang, X. Li, H. Wang, J. Guo, H. Dai, *Phys. Rev. Lett.* **2008**, *100*, 206803.
- [4] F. Schwierz, *Nat. Nanotechnol.* **2010**, *5*, 487.
- [5] C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, *Science* **2006**, *312*, 1191.
- [6] S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **2007**, *7*, 3394.
- [7] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
- [8] H. Yamaguchi, G. Eda, C. Mattevi, H. K. Kim, M. Chhowalla, *ACS Nano* **2010**, *4*, 524.
- [9] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706.
- [10] C. Lee, S. Baik, *Carbon* **2010**, *48*, 2192.
- [11] S. Wang, P. K. Ang, Z. Wang, A. L. L. Tang, J. T. L. Thong, K. P. Loh, *Nano Lett.* **2009**, *10*, 92.
- [12] Y. Lee, S. Bae, H. Jang, S. Jang, S. E. Zhu, S. H. Sim, Y. I. Song, B. H. Hong, J. H. Ahn, *Nano Lett.* **2010**, *10*, 490.
- [13] M. Y. Han, B. Özyilmaz, Y. Zhang, P. Kim, *Phys. Rev. Lett.* **2007**, *98*, 206805.
- [14] Z. H. Ni, T. Yu, Y. H. Lu, Y. Y. Wang, Y. P. Feng, Z. X. Shen, *ACS Nano* **2008**, *2*, 2301.
- [15] X. Gao, J. Jang, S. Nagase, *J. Phys. Chem. C* **2009**, *114*, 832.
- [16] S. Park, Y. Hu, J. O. Hwang, E.-S. Lee, L. B. Casabianca, W. Cai, J. R. Potts, H.-W. Ha, S. Chen, J. Oh, *Nature Commun.* **2012**, *3*, 638.
- [17] O.-K. Park, Y.-M. Choi, J. Y. Hwang, C.-M. Yang, T.-W. Kim, N.-H. You, H. Y. Koo, J. H. Lee, B.-C. Ku, M. Goh, *Nanotechnology* **2013**, *24*, 185604.
- [18] M. Cheng, R. Yang, L. Zhang, Z. Shi, W. Yang, D. Wang, G. Xie, D. Shi, G. Zhang, *Carbon* **2012**, *50*, 2581.
- [19] V. López, R. S. Sundaram, C. Gómez-Navarro, D. Olea, M. Burghard, J. Gómez-Herrero, F. Zamora, K. Kern, *Adv. Mater.* **2009**, *21*, 4683.
- [20] R. M. Pasquarelli, D. S. Ginley, R. O'Hayre, *Chem. Soc. Rev.* **2011**, *40*, 5406.
- [21] V. H. Pham, T. V. Cuong, S. H. Hur, E. W. Shin, J. S. Kim, J. S. Chung, E. J. Kim, *Carbon* **2010**, *48*, 1945.
- [22] X. Wang, L. Zhi, K. Müllen, *Nano Lett.* **2008**, *8*, 323.
- [23] S. Watcharotone, D. A. Dikin, S. Stankovich, R. Piner, I. Jung, G. H. B. Dommett, G. Evmenenko, S. E. Wu, S. F. Chen, C. P. Liu, *Nano Lett.* **2007**, *7*, 1888.
- [24] H. A. Becerril, J. Mao, Z. Liu, R. M. Stoltenberg, Z. Bao, Y. Chen, *ACS Nano* **2008**, *2*, 463.
- [25] J. T. Robinson, M. Zalalutdinov, J. W. Baldwin, E. S. Snow, Z. Wei, P. Sheehan, B. H. Houston, *Nano Lett.* **2008**, *8*, 3441.
- [26] J. Wu, H. A. Becerril, Z. Bao, Z. Liu, Y. Chen, P. Peumans, *Appl. Phys. Lett.* **2008**, *92*, 263302.
- [27] L. T. Le, M. H. Ervin, H. Qiu, B. E. Fuchs, W. Y. Lee, *Electrochem. Commun.* **2011**, *13*, 355.
- [28] E. Irissou, J. G. Legoux, A. N. Ryabinin, B. Jodoin, C. Moreau, *J. Therm. Spray Technol.* **2008**, *17*, 495.
- [29] Y. U. Ko, S. Cho, K. S. Choi, Y. Park, S. T. Kim, N. H. Kim, S. Y. Kim, S. T. Chang, *J. Mater. Chem.* **2012**, *22*, 3606.
- [30] R. Nigmatullin, *Dynamics of Multiphase Systems*, Vol.1–2, Hemisphere, Washington **1990**.
- [31] N. Ashgriz, *Handbook of Atomization and Sprays*, Vol.11, Springer, New York **2011**.
- [32] A. Yarin, G. Brenn, O. Kastner, D. Rensink, C. Tropea, *J. Fluid Mech.* **1999**, *399*, 151.
- [33] A. Dato, V. Radmilovic, Z. Lee, J. Phillips, M. Frenklach, *Nano Lett.* **2008**, *8*, 2012.
- [34] P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, *Nano Lett.* **2008**, *8*, 1704.
- [35] D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **2008**, *3*, 101.
- [36] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, *3*, 270.
- [37] M. Lotya, P. J. King, U. Khan, S. De, J. N. Coleman, *ACS nano* **2010**, *4*, 3155.
- [38] S. Bae, H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, *Nat. Nanotechnol.* **2010**, *5*, 574.
- [39] A. Ferrari, J. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. Novoselov, S. Roth, *Phys. Rev. Lett.* **2006**, *97*, 187401.
- [40] R. Zan, Q. M. Ramasse, U. Bangert, K. S. Novoselov, *Nano Lett.* **2012**, *12*, 3936.

- [41] P. Jacobson, B. Stoger, A. Garhofer, G. S. Parkinson, M. Schmid, R. Caudillo, F. Mittendorfer, J. Redinger, U. Diebold, *J. Phys. Chem. Lett.* **2011**, 3, 136.
- [42] H. Wang, J. T. Robinson, X. Li, H. Dai, *J. Am. Chem. Soc.* **2009**, 131, 9910.
- [43] F. Tuinstra, J. L. Koenig, *J. Chem. Phys.* **1970**, 53, 1126.
- [44] K. N. Kudin, B. Ozbas, H. C. Schniepp, R. K. Prud'Homme, I. A. Aksay, R. Car, *Nano Lett.* **2008**, 8, 36.
- [45] A. C. Ferrari, *Solid State Commun.* **2007**, 143, 47.
- [46] D. R. Lenski, M. S. Fuhrer, *J. Appl. Phys.* **2011**, 110, 013720.
- [47] M. Rahaman, A. F. Ismail, A. Mustafa, *Polym. Degradation Stab.* **2007**, 92, 1421.
- [48] R. Setnescu, S. Jipa, T. Setnescu, W. Kappel, S. Kobayashi, Z. Osawa, *Carbon* **1999**, 37, 1.
- [49] B. Kumar, M. Asadi, D. Pisasale, S. Sinha-Ray, B. A. Rosen, R. Haasch, J. Abiade, A. L. Yarin, A. Salehi-Khojin, *Nature Commun.* **2013**, 4, 2819.