Reducing sheet resistance of self-assembled transparent graphene films by defect patching and doping with UV/ozone treatment

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Highlights

- Photochemical oxidation (UV/ozone treatment) of self-assembled solution-processed graphene films is demonstrated for the first time
- The effect that photochemical oxidation has on self-assembled graphene film is a reduction of sheet resistance, the opposite of the earlier reported effect on CVD or mechanically exfoliated graphene
- Edges as the dominant defect type in self-assembled graphene films play a crucial role in the presented defect density decrease
- Photochemical oxidation is proposed as a method of increasing the carrier mean free path, doping, and lowering sheet resistance of solution-processed graphene films
Abstract

Liquid phase exfoliation followed by Langmuir-Blodgett self-assembly (LBSA) is a promising method for scalable production of thin graphene films for transparent conductor applications. However, monolayer assembly into thin films often induces a high density of defects, resulting in a large sheet resistance that hinders practical use. We introduce UV/ozone as a novel photochemical treatment that reduces sheet resistance of LBSA graphene threefold, while preserving the high optical transparency. The effect of such treatment on our films is opposite to the effect it has on mechanically exfoliated or CVD films, where UV/ozone creates additional defects in the graphene plane, increasing sheet resistance. Raman scattering shows that exposure to UV/ozone reduces the defect density in LBSA graphene, where edges are the dominant defect type. In addition, work function measurements reveal that the treatment dopes the LBSA film, making it more conductive. Such defect patching paired with doping leads to an accessible way of improving the transparent conductor performance of LBSA graphene, making solution-processed thin films a candidate for industrial use.

Keywords: Graphene films, Liquid phase exfoliation, Langmuir-Blodgett assembly, UV/ozone treatment, Defect patching, Transparent conductors

1. Introduction

Graphene, with its high optical transparency and low sheet resistance, is an excellent choice for transparent electrodes in various optoelectronic devices [1]. For such applications, transparency in the visible part of the spectrum should be above 80%, while the sheet resistance should be low enough for practical use, all while keeping production costs to a minimum. In the past decade,
numerous research efforts were performed to achieve production of thin graphene films usable in practical applications [2-4]. Although chemical vapor deposition (CVD) yields graphene sheets of high quality that can be scaled for industrial use [5], the method is generally regarded as costly [6] and alternative methods are being sought that satisfy the quality/cost tradeoff. Liquid phase exfoliation (LPE) [7] is the most perspective way of obtaining large quantities of exfoliated graphite in solution at reasonable production costs. Nevertheless, all solution-processed graphene needs to be controllably assembled into thin films of satisfactory quality for transparent conductor applications. A number of film assembly strategies exist, such as evaporation-based assembly, assisted, and micropatterned assembly [8]. Each specific thickness and arrangement of graphene sheets in a thin film directly affects physical properties of the film [9] and device performance. Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) deposition, based on surface-tension induced self-assembly of nanoplatelets at an interface of two liquids or a gas and a liquid, are prime candidate methods for production of large-scale, highly transparent thin graphene films [10-11]. However, all self-assembled films suffer from a large density of defects that often leads to a high sheet resistance of deposited film. Conversely, the large defect density offers an opportunity for surface treatment such as annealing, chemical doping and functionalization [3, 12], all of which can reduce sheet resistance or produce other desirable effects. The susceptibility of a film to treatment as well as its initial sheet resistance depend on the nature of the prevalent defects, such as impurities, vacancies, nanoplatelet edges, and topological defects, as well as the defect density. For example atoms located at the edges of a graphene sheet exhibit higher reactivity compared to those in the basal plane, making the ratio of the density of edge atoms to basal-plane atoms the determining factor for the efficiency of surface modification [13]. It is thus imperative to carefully study the nature and density of
defects in any thin film transparent conductor, especially when considering physical or chemical
treatment to enhance the film’s practical usability.

Here, we report characterization of the defect type of Langmuir-Blodgett self-assembled
(LBSA) films from LPE graphene and subsequent defect patching with UV/ozone (UVO)
treatment. We monitored the photochemical oxidation reaction of our films exposed to ozone, a
very important gas adsorbate that significantly alters the properties of materials through doping,
affecting the performance of electronic devices, usually limiting their use [14-15]. As already
shown, oxidation spreads from edges across the entire surface of graphene flakes [16]. Applied
to mechanically exfoliated and monolayer CVD graphene photochemical oxidation, even during
a relatively short time, leads to significant defect generation resulting in an increase of sheet
resistance [17, 18]. Ozone reacts with the edge sites of CVD graphene until a saturation point is
reached. After that the basal plane becomes more susceptible to oxidation, resulting in the
replacement and relief of carbon atom defects. We find that nanoplatelet edges are the dominant
defect type in our films, in contrast to CVD-grown graphene and earlier reported mechanically
exfoliated graphene, where charged impurities and covalently bonded adatoms are the limiting
factor for carrier mobility [19]. In this paper, we treat the film surface with ultraviolet radiation
and ozone and find that the sheet resistance decreases by a factor of 3, while optical transparency
throughout the visible part of the spectrum remains high (>80%) and virtually unchanged.
Measurements of the surface work function indicate that doping is responsible for the decrease in
sheet resistance. With a careful analysis of Raman spectra, we find that the density of defects
decreases with treatment, yielding an increase in the carrier mean free path, while edges remain
the dominant defect type, all indicating that the ozone binds predominantly to the edges of
graphene nanoplatelets. We perform the same UVO treatment on CVD graphene and show that
on monolayer CVD graphene, UVO has a detrimental effect on sheet resistance. We also treat thick CVD-grown multilayer graphene films, which prove to be robust against UVO treatment, although such films have very low optical transparency. Furthermore, in order to understand the experimental results we theoretically analyze deposition of an ozone molecule on the edges of a wide graphene nanoribbon (GNR) as a nanosystem that well approximates LBSA film. After we determine the deposition mechanism, we present electronic and transport properties of such oxidized ribbons. We thus conclude that UVO treatment is a good option for reducing sheet resistance of LBSA LPE graphene films, bringing the electronic performance of these sheets closer to that of CVD graphene which is produced at a higher cost.

2. Methods

A graphene dispersion was prepared from graphite powder (Sigma Aldrich, product no. 332461) from a concentration of 18 mg ml-1 in N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, product no. 328634), exposed to 14 hours of sonication in a low-power sonic bath. The resulting dispersion was centrifuged for 60 min at 3000 rpm in order to reduce the concentration of unexfoliated graphite. The resulting dispersions were used to form films approximately 3 nm thick by LBSA, in the same way that we demonstrated in our previous work [12, 20]. A small amount of graphene dispersion is added to a water-air interface and after the film is formed, it is slowly scooped onto the target substrate (Figure 1a). Glass and SiO2/Si are used as substrates.

For single-layer CVD studies, we used commercially available monolayer CVD graphene grown on 20 μm thick copper foil (Graphene Supermarket) and transferred onto SiO2/Si substrate with a home-built automatic transfer system using ammonium persulfate ((NH4)2S2O8) 0.3M as copper etchant [21]. For multilayer CVD studies, we used multilayer graphene with an average
thickness of 105 nm (about 300 monolayers) grown on 25 μm-thick nickel foil (Graphene Supermarket). We etched away the nickel foil in 0.25 M solution of ferric chloride (FeCl$_3$) in water, yielding a floating multilayer graphene film which was scooped out of the solution onto a SiO$_2$/Si substrate in the same way as already reported for multilayer graphene condenser microphones [22].

Photochemical oxidation (UVO treatment) is performed by exposing the graphene films to ultraviolet radiation and ozone for 3, 5, 15 and 30 min at a 50°C chamber temperature and ambient pressure in a Novascan UV/ozone Cleaner by converting oxygen from ambient air to ozone using a high intensity mercury lamp (Figure 1b).

For optical characterization, UV-VIS spectra were taken using a Perkin-Elmer Lambda 4B UV/VIS Spectrophotometer. The oxidation process was characterized using a TriVista 557 S&I GmbH Micro Raman spectrometer ($\lambda = 532$ nm) at room temperature. The resistance of each sample was measured in a two-point probe configuration and the sheet resistance was obtained by including sample geometry factors. The work function measurement is performed using Kelvin probe force microscopy (KPFM, NTEGRA Spectra), prior to and after photochemical treatment of our graphene films.

The calculations are done using density functional-based tight binding method (DFTB) [23, 24] with self-consistent charge correction as implemented in the DFTB+ code [25]. Spin polarization was included in calculations. This method has a proven record of various applications to graphene and graphene nanoribbons [26-29]. Transport properties are calculated by DFTB augmented with the Green’s functions formalism [30]. Since the atomic structure of LBSA graphene is dominated by edges, we find GNR as a suitable nanosystem with physical properties probably converging to those of nanoflakes obtained in the presented experiments. For
this purpose a wide GNR with width of around 2 nm is utilized. The interaction between electronic clouds of two GNR edges is small for such a wide ribbon, hence its electronic properties are equal to asymptotic limit of wide ribbons [31]. The periodic (infinite) edges of GNR correspond to the flakes in the experiment, which have large circumferences, i.e. long edges. Utilization of the GNR instead of nanoflake per se is not only physically equivalent but also numerically much more tractable.

3. Results and discussion

Figure 2a depicts the sheet resistance of graphene films upon exposure to UVO. Prior to exposure, the sheet resistance of LBSA graphene (red circles) is above 80 kΩ/sq. Upon exposure, the sheet resistance decreases rapidly within the first 5 min, reaching a value below 30 kΩ/sq, an approximately 3-fold reduction. At those exposure levels, oxidation reaches a saturation point and remains stable for longer exposure times. Single layer CVD graphene exhibits a pronouncedly different behavior (violet circles), starting from a very low value of sheet resistance which gently rises after 5 mins of exposure, dramatically increasing for longer exposures. After 5 minutes of treatment, sheet resistance of CVD graphene is still 3-4 times less than that of LBSA graphene. At exposure times of ~10 minutes, the resistance of the two sheets equates, whereas for a 30 minute treatment it is the LBSA graphene that exhibits 4 times smaller resistance values. Multilayer CVD graphene (blue circles) has a sheet resistance of ~ 8 kΩ/sq, which changes only slightly even for long exposures to UVO.

It is expected that CVD graphene compared to LBSA graphene boasts a lower sheet resistance, which is inherently related to carrier mobility. Carrier mobility is inversely proportional to the density of scattering defects, which should be small in CVD graphene. LBSA
graphene morphology has an abundance of nanoplatelet edges [20] that act as scattering centers and have a detrimental effect on initial sheet resistance. However, with UVO treatment, that resistance decreases, pointing to a reaction of ozone with existing defects [16]. In CVD graphene, a few edge sites are fully saturated by ozone molecules in a short period of time, allowing ozone molecules to deposit their energy in the formation of defects or in adsorption, thus creating new point defects at the basal plane that have a detrimental effect on sheet resistance [18]. In multilayer graphene, UVO has little effect on sheet resistance because the ozone molecules react with the top layers only, whereas charge transport takes place through the entire volume of the sheet.

To examine the origins of reduced sheet resistance with UVO treatment, we measure the surface work function (WF) with KPFM. Figure 2b depicts KPFM maps of the contact potential difference (CPD) between the sample and the tip, before and after UVO exposure. Note the different colormap scale, that indicates a lower CPD between the doped sample and the metallized AFM tip for treated samples compared to untreated samples. To measure the absolute value of the WF, we use as a reference the work function of highly ordered pyrolytic graphite (HOPG), a tabulated value of 4.6 eV [32, 33]. In order to determine the average CPD of the measured surface, histograms of KPFM maps were used and fitted to a Gaussian distribution (Figure 2c). The mean WFs of the tip, HOPG, untreated, and treated films are plotted against the vacuum level in Figure 2d. The exact procedure is detailed in our previous work [20]. It is evident that UVO treatment increases the WF from 4.8 eV to 4.9 eV, shifting the Fermi level downwards by 100 meV. It is this additional UVO-induced p-doping that leads to an increased carrier concentration, in turn causing decreased sheet resistance [34].
Aside from improving the sheet resistance, for transparent conductor applications it is important that the optical transparency of the treated film remains high. Figure 3a depicts AFM topography of the same areas of the film that were used to measure the WF. No difference is observed in the film morphology as an effect of UVO exposure. Figure 3b depicts the transmittance spectrum of the pristine and treated UVO film. The film has good transparency throughout the visible part of the spectrum, with 80-85% transmittance. The transmittance of the film is barely affected by the treatment. For comparison, monolayer CVD would have transmittance on the order of ~97%, whereas multilayer CVD transmits under 10% of light in the visible, according to manufacturer specifications. Hence, single layer CVD graphene has the overall best performance for transparent conductor applications, although cost remains a limiting factor for wide-scale use, whereas multilayer CVD has little use for such applications due to its low transparency. LBSA graphene holds the middle ground, with acceptable electronic and optical performance (especially after UVO treatment) with projected low costs of fabrication and good scalability. It is important to note that the unchanged transparency coupled with a reduced sheet resistance leads to a threefold increase in the figure of merit (FOM) for transparent conductor applications [35].

The opposite effect that UVO has on CVD and LBSA graphene demands an inquiry into the effect of reactive site morphology on reactions with ozone. LBSA graphene morphology is dominated by nanoplatelet edge defects, whereas CVD yields graphene that has a few edges, in which chemical reactions should be governed by point defects such as charged impurities and covalently bonded adatoms [35]. To clarify the nature of reactive defects and their evolution during UVO treatment, we apply Raman spectroscopy, a versatile tool for characterization of graphene-based materials [36].
Figure 4a depicts Raman spectra of LBSA graphene as a function of UVO exposure. The spectra feature four pronounced bands: D at ~1343 cm\(^{-1}\), G at ~1579 cm\(^{-1}\), D' at ~1614 cm\(^{-1}\) and the 2D band at ~2694 cm\(^{-1}\). Furthermore, several combinations of these bands are also observed: D + D'' at ~2450 cm\(^{-1}\) and D + D' at ~2935 cm\(^{-1}\) (Figure 4b), where D'' is signature of a phonon belonging to the LA branch, typically seen at ~1100 cm\(^{-1}\) \[36\]. The D and G bands are well resolved for all samples. The 2D peak is a typical signal arising in multilayer graphene. However, Raman spectra show evident changes of the intensity of the D mode with UVO exposure. Figure 4c depicts the ratio of the D peak to the G peak calculated from integrated peak areas, often used to monitor defect evolution in graphene. We observe a large decrease of this ratio during UVO exposure, indicating a reduction in defect density. The D/G intensity ratio evolution shows the same trend as sheet resistance, with a rapid change within the first 5 minutes of exposure, followed by a saturation behavior. The reduction of defect density with UVO exposure in LBSA graphene is opposite from our results on CVD graphene (Figures S1 and S2) and the literature on monolayer graphene \[12-13\]. LBSA graphene thus responds in a unique way to an oxidizing environment, with ozone binding to existing defects leading to improved electrical performance.

The ratio \(I_D/I_G\) can be converted to the carrier mean free path (\(L_D\)), as long as the laser wavelength is known \[37\]:

\[
L_D^2 (nm)^2 = (1.8 \pm 0.5) \times 10^{-9} \lambda_L^4 \left(\frac{I_D}{I_G}\right)^{-1} \tag{1}
\]

For the wavelength used in this study (\(\lambda_L=532\)nm), we plot \(L_D\) as a function of exposure time in Figure 4d. \(L_D\) in LBSA graphene increases from 15 nm to 19.5 nm upon UVO exposure, again indicating defect patching. Before and after exposure, the mean free path is smaller than our
average flake diameter (previously reported as 120 nm [20]), which points to defects within the nanoplatelets, either through edges of sheets that are stacked on top of each other, or through other point-like defects that we cannot observe with AFM and SEM.

Possible defects in graphene include topological defects (such as pentagon-heptagon pairs), boundaries, vacancies, substitutional impurities, and sp$^3$ defects [38]. Topological defects have the lowest formation energy [39], and they are always present in LPE graphene sheets as a result of the cavitation process [40]. As the ratio between the intensity of the D and the D' mode is very sensitive to the type of defect, with a value of 3.5 for edges, 7 for vacancies, between 7 and 13 for substitutional impurities, and 13 for sp$^3$ defects [41, 42], we measure this value to deduce the nature of defects in our sample. We observe that the ratio of the D-peak intensity to the D’-peak intensity in our films is a roughly constant at a value of 4.8±0.5 regardless of UVO exposure. The measured ratio indicates that edges are the dominant defect type in our films, ruling out vacancies, substitutional impurities, and sp$^3$ defects, in agreement with previously published data for LPE graphene [40]. There is little change in defect type with photochemical oxidation (Figure 4e), although the defect density decreases, indicating that ozone most likely reacts with the existing defects and patches them.

In LBSA graphene, flakes may bundle in stacks with varying thickness and lateral dimensions, edge geometries and their saturations with oxygen hydrogen or chemical groups, and a wide variety of possible defects. From these virtually infinite possibilities and due to the absence of microscopic experimental data on atomic structure we choose an example of a GNR with bare zig-zag edges and with width of 2 nm for our DFTB+ calculations. Electronic properties of graphene depend sensitively on physical and chemical modification of edges [43-45]. It was shown that roughness at zig-zag edges does not significantly influence their
conductance in contrast to armchair edges [46-48]. The simple choice of a zig-zag GNR is for demonstration purpose only, i.e. to uncover the basic physics of the experimental results, without intent to cover all aspects of the experimental reality. The initial atomic structure consists of the GNR with an ozone molecule placed parallel to the edge. After geometry optimization of the system we obtained a transition configuration (TC) using the dimer method [49]. Optimization of the TC geometry led to the next (meta)stable geometry. The nudged elastic band (NEB) method [50, 51] is used for evaluation of the potential barrier between the configurations. Using this procedure we obtained three (meta)stable configurations. The reaction is presented in Figure 5a and 5b. Firstly, one of the two O-O bonds in O₃ breaks, which is followed by a rotation of the O-O dimer around a C-C axis by 180°, as illustrated with the insets in Figure 5a. The product of the reaction is the GNR edge with three separate O adatoms at the nearest sites of the edge (the configuration will be called 3O in the remaining text). The potential barrier for the reaction is Eᵣ = 1.11 eV, while the energy for the reverse reaction is Eᵣ = 4.58 eV. At the temperature of 50°C, which was used in our experiment, both forward and reversed reactions are impossible. However, the exposure of the sample to the UV radiation may assist the reaction. The forward reaction is exothermic with ΔE = -3.47 eV. Two of the three O atoms attached at the edge can associate into an O₂, as indicated in Figure 5b. The potential barrier is much smaller in this case, being only Eᵣ = 0.05 eV. The reversed reaction is also viable with Eᵣ = 0.22 eV. The reaction is exothermic as well, with ΔE = -0.17 eV. The final product of the cascaded reaction consisting of an O₂ molecule and an adatom at the GNR edge will be designated as O₂+O configuration in following text. Therefore both configurations, O₂+O and 3O, being nearly isoenergetic, can coexist at the same time. The reaction is somewhat different from the one obtained in [52], but it
is expected since the paper considered zig-zag edge in a small hydrogenated carbon cluster in contrast to the infinite ribbon without edge saturation in our research.

The conductance of the three configurations (the initial one, O$_3$, and the two reaction products O$_2$+O and 3O) is shown in Figure 5c. While a pristine zig-zag GNR (not shown in the figure) does not have electronic gap, it opens upon deposition of O$_3$ at a GNR edge. The Fermi level (EF) is placed at the top of the valance band in the initial O$_3$ and O$_2$+O configurations. The electronic gaps are around 0.10 eV and 0.35 eV, respectively, whereas the conductance at EF is one quantum for both cases. This corresponds to around 12.9 kΩ. Breaking of the O-O bond in the O$_2$+O configuration causes a significantly different conductance. The 3O configuration does not exhibit a gap, while the conductance is increased by a factor of 3 or 5, since EF is positioned at the border of regions with two distinct conductance values. The 3- to 5- fold increase of conductance of a free-standing GNR indicates a possible mechanism of increase in LBSA film conductance in our experiment. Note that it is not one-to-one correspondence as transport through the LBSA graphene is more complex, involving stacks of GNRs of a variety of GNR edges, and transport between stacks which is perhaps based on quantum tunneling. However the increase of conductance is rather in positive correlation with our experiments. All configurations exhibit a p-type doping, in agreement with experiment.

A complete analysis of electronic properties of stacks of flakes (or GNRs) would require consideration of flakes with numerous combinations of edge structures, physical dimensions of flakes and their different mutual orientations, varying number of GNRs in stacks. After obtaining the conductance inside and between stacks a set of stacks could be modeled with an equivalent electrical circuit and their resistance calculated. This comprehensive study will be published elsewhere. Here, for demonstration only, we opt for a single structure, a Bernal stacking of four
GNRs with an O$_2$+O edge configuration as shown in Figure 5d. We compare projected density of states (PDOS) of the stack without and with oxidation in plane of the top layer in Figure 5e and 5f, respectively. The O adatoms responsible for the in-plane oxidation make epoxy groups as found previously in [53]. Upper four sub-graphs in each panel represent PDOS at the GNR edge, while the lower four sub-graphs show PDOS at the center of GNR. Colors of the graphs distinguish four GNRs in the stack (named layers in Figure 5e and 5f). Both edges and middle of GNRs contribute to PDOS in the range from $E_F - 0.5$ eV to $E_F + 0.5$ eV. Edges have much larger contributions for energies below $E_F - 0.5$ eV, hence conductance is expected to be dominated by edges for a bias voltage larger than $\sim 1$V. The stack without in-plane oxidation exhibits a uniform PDOS among layers, with $E_F$ positioned at the top of the valence band. In contrast, the oxidation of the top layer alternatively dopes the layers with p and n character. Since PDOS at $E_F$ is non-zero in three out of four layers, we expect a much larger low-bias conductance of the in-plane oxidized stack than the one without in-plane oxidation. Note that the transport properties analyzed in this section are applicable only to the plane parallel to GNRs in the stack. The conductance in the perpendicular direction has rather a tunneling character, with expected much larger electric resistance.

4. Conclusion

In contrast to the degrading effects it has on CVD graphene, photochemical oxidation (UV/ozone treatment) of LBSA graphene leads to a decrease in defect density, which together with doping reduces sheet resistance while retaining high optical transparency. We find that edges are the dominant defect type in LBSA graphene, with little influence of other defects such as vacancies, impurities, or sp$^3$ defects that are common limiting factors for electronic performance of CVD and mechanically exfoliated graphene. Our study thus shows that graphene film morphology and
defect landscape play a crucial role in the effect that UV/ozone treatment has on the film. This accessible treatment improves the performance of LBSA graphene, which is key to embedding such materials in durable devices especially those involving direct exposure to ultraviolet radiation and ozone gas. Our novel observation is expected to contribute to the technological acceptance of thin films based on solution-processed 2D materials.

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List of figures

Figure 1 (a) Schematic of Langmuir-Blodgett self-assembly (LBSA) on a water-air interface (1: film formation, 2: substrate immersion, 3: film deposition), NMP is N-Methyl-2-pyrrolidone; (b) Schematic of film exposure to photochemical oxidation.

Figure 2 a) Sheet resistance of LBSA, CVD-grown single- and multilayer graphene films as a function of UVO exposure time, b) KPFM map of HOPG, untreated, and UVO treated LBSA film, (c) KPFM histograms of LBSA graphene film before (grey) and after (red) UVO treatment, (c) Schematic of the relation between measured CPDs and their corresponding work functions.

Figure 3 (a) 3x3 µm² topograph of HOPG, untreated, and UVO treated LBSA film, b) Transmittance of a LBSA graphene film in the visible range on a glass substrate, before (black) and after (red) 5 min exposure to UVO.

Figure 4 (a) Representative Raman spectra of LBSA graphene as a function of UVO exposure time. We recorded Raman spectra in various regions to eliminate spot-to-spot variations in the obtained spectra. The spectra show four main bands: D, G, D’, and 2D, as well as some weak combinations of these modes. (b) Close-up view of the main bands, (c) The D/G intensity ratio of the films as a function of UVO exposure. The D/G ratio is calculated from integrated peak areas. (d) Interdefect distance as a function of UVO exposure time. The error bar represents the standard deviation of five measurements, (e) The D/D’ ratio as a function of UVO exposure time.

Figure 5 (a) and (b) Potential energy surface of the cascaded reaction of an O₃ molecule with a GNR zig-zag edge (O₃ configuration). Breaking of an O-O bond in the ozone molecule and rotation of O-O dimer about C-O dimer (transition state), which settles the intermediate (3O)
state, are shown in (a). The consequent association of two neighboring O atoms, yielding the O$_2$+O configuration, is presented in (b). The reaction is analyzed only on one edge (the left edge in the insets). (c) Conductance at zero bias of the GNR with the three configurations. (d) Illustration of the stack with four layers of GNRs with O$_2$+O edge configuration doped in-plane by five oxygen atoms. Projected density of states of the stack without (e) and with (f) in-plane doping are shown for the stack. Panels (e) and (f) distinguish contributions to PDOS from GNR edges and lines of central carbon atoms.
Figures

Figure 1

Figure 2
Figure 5
Supplementary information

UV/Ozone patching of edge defects for reduced sheet resistance of transparent self-assembled graphene films

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UV/Ozone treatment was performed on CVD single- and multilayer graphene. Corresponding Raman spectra are shown in Figure S1.

**Fig. S1**  (a) Raman spectra of the LBSA, CVD-grown multilayer and CVD-grown single-layer graphene films as a function of UVO exposure time, (b) Close-up view of the main bands of (a).

In all cases, Raman spectra show evident changes of the intensity of the D mode with photochemical oxidation. Figure S1 highlights the different behavior of LBSA and CVD graphene in an oxidizing environment. In contrast to the effect that UVO has on LBSA graphene, described in the main text, treatment of CVD graphene leads to defect generation. Upon photochemical oxidation, CVD graphene develops a strong D peak in the Raman spectra after only 5 min of exposure, indicating oxidative removal of the graphitic material and the formation of a significant number of defects. Figure S2a shows a comparison of the ratio of the D-peak to
the G-peak before and after UVO exposure for LBSA, CVD multilayer and CVD single-layer graphene. As already mentioned, a large decrease of this ratio is observed after UVO exposure for LBSA graphene and an increase of this ratio is observed after the same time of exposure for CVD graphene, indicating defect patching in LBSA and defect formation in CVD. Figure S2b shows a change in the mean free path with UVO exposure of all three types of graphene.

**Fig. S2** (a) The D/G intensity ratio of the LBSA, CVD-grown multilayer and CVD-grown single-layer graphene films as a function of UVO exposure time. The D/G ratio is calculated from integrated peak areas. (b) Interdefect distance of the corresponding graphene films as a function of UVO exposure time. The error bar represents the standard deviation of five measurements.
