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## **Fabrication of Chemical Graphene Nanoribbons** via Edge-Selective Covalent Modification

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The excellent properties of graphene, including high carrier mobility (200 000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>), <sup>[1]</sup> high thermal conductivity  $(5300 \text{ W m}^{-1} \text{ K}^{-1})$ ,<sup>[2,3]</sup> and optical transparency (97.7%),<sup>[4]</sup> make it a promising material for future electronics. However, the gapless nature of graphene limits its application in standard logic circuit as a candidate for post-silicon electronics. Tremendous efforts have been devoted to open the bandgap of graphene, for example, chemical modification<sup>[5-9]</sup> and applying a perpendicular electric field on bilaver graphene.<sup>[10–13]</sup> Among the techniques reported, fabrication of graphene nanoribbons (GNRs)<sup>[14-19]</sup> is considered as one of the most promising methods. Because of the quantum confinement and edge effects,<sup>[20,21]</sup> such GNRs with nanometer-sized width are endowed with tunable bandgaps and high on/off ratios, facilitating the development of GNR-based electronics. So far, a number of techniques for the fabrication of geometrically isolated GNRs have been reported,<sup>[22,23]</sup> including both top-down (such as lithographic,<sup>[14,24]</sup> sonochemical,<sup>[16,25]</sup> and chemical cutting of graphene,<sup>[26,27]</sup> as well as unzipping of carbon nanotubes<sup>[18,19,28]</sup> and bottom-up (such as direct chemical vapor deposition growth<sup>[29,30]</sup> and chemical synthesis<sup>[31]</sup>) strategies. Among these methods, lithographic patterning followed by plasma etching is popular for the industry-amenable large-scale production. However, because of the disordered edges induced by the oxygen etching, the conductivity of GNRs obtained from lithographic method is usually not high enough,<sup>[15]</sup> which is quite depressing. Though bottom-up methods do not suffer from such a disordered edge issue, those methods are often sophisticated, low-yield and tending to aggregate in the liquid phase reaction, not to mention the incapability to produce long GNRs. Unlike the geometrically nanometer-width GNRs, chemical graphene nanoribbons (CGNRs) are nanosized conducting ribbons chemically isolated by the insulating modified edges. In other words, a CGNR may have a much larger geometrical width but a nanometer-scale electrical conduction channel. Compared with the rough edges of ordinary GNRs, such kind of smooth chemical edges in CGNRs is expected to bring about high electrical performances.<sup>[32,33]</sup> Moreover, the properties of CGNRs could be tuned by varying the functional groups chemically bonded onto the graphene basal plane.<sup>[32]</sup> Such kind of

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CGNRs may provide an alternative route for fabricating highperformance electronic devices. Therefore, an effective method for fabricating CGNRs is highly desired.

In previous work,<sup>[34]</sup> we discovered that the chemical reaction of graphene with di-tert-butyl peroxide (DTBP) was highly edge-selective as shown in Scheme 1. The methyl radicals released from DTBP molecules were preferentially attacking the graphene edge, inducing a progressive edge-to-center covalent modification of graphene.<sup>[35]</sup> This edge-selective reaction established the chemical basis for fabricating CGNRs. In this work, starting from a wide graphene ribbon (WGR), the electrical conduction channel of graphene is gradually narrowed down simply by controlling the above photomethylation reaction time. The CGNRs have nanometer-scale native graphene conduction channels embedded into the insulating methylated graphene. Thus fabricated CGNRs exhibit current on/off ratios varying from 100 to 10<sup>4</sup>, indicating a wide and tunable bandgap. High-performance field effect transistors have been made based on these CGNRs, which opens up a new avenue for creating next generation graphene-based electronic devices.

Generally, CGNRs were fabricated using WGRs as the starting material. In a typical reaction, microsized graphene flakes were first mechanically exfoliated onto silicon substrate through the Scotch-tape method. A standard electron beam lithography process was then carried out, followed by plasma etching treatment. WGRs with widths ranging from 300 nm to 1 µm were thus obtained (Figure 1a). After that, 5 nm Cr and 50 nm Au were successively thermally deposited on the graphene sample as electrical contacts. Such WGR-based devices were then immersed in the DTBP liquid and a mercury lamp (20 mW, wavelength from 320 to 500 nm) was utilized to trigger the photochemical reaction between graphene and DTBP. With the edge-to-center progressive methylation, CGNRs were finally prepared.

Raman spectroscopy was used to investigate the structure of graphene samples. For WGRs, a small D band was observed



Scheme 1. a) Photomethylation reaction of graphene with di-tert-butyl peroxide. b) Schematic structure of a chemical graphene nanoribbon, formed by an edge-to-center progressive methylation of graphene.

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**Figure 1.** a) Optical microscope images of a WGR-based device. The inset is the AFM image of the area in the black square, and the scale bar is 500 nm. Raman spectra of WGR's edge and center b) before reaction, c) after 5-min reaction, and d) after another 5-min reaction. The inset images are the D band mapping results, and the scale bar is 300 nm.

on the edge before reaction (Figure 1b, black curve), indicating the presence of slightly oxidized graphene edge (1–3 nm) originating from the plasma-etching process.<sup>[36–38]</sup> The uniform but low D band intensity in the Raman mapping result (inset of Figure 1b) suggested the pristine nature of the center region of WGR. After WGRs were immersed into the DTBP liquid for 5 min, a strong D band arose in the edge region while the center area remained almost unchanged, confirming the higher reactivity of the graphene edge area (Figure 1c). After another 5-min reaction, a high and uniform D band intensity was observed for the whole graphene sample (Figure 1d), indicating the extension

of methylation from the edge to the center as predicted. Therefore, by controlling the reaction time, the width of CGNRs could be well tuned.

Considering the limited spatial resolution (over 100 nm), Raman mapping cannot give a direct evidence of the nanometersized CGNRs. For this reason, careful and detailed transport measurements were conducted to monitor the reaction process, thus revealing the width of CGNRs. Typically, the highly doped *p*-type silicon supporting substrate (<0.004  $\Omega$  cm) was used as back gate, while the 300 nm thermal oxide layer was used as the gate dielectrics. The transport measurement for WGR-based device with 300 nm width and 3 µm length was carried out at room temperature and ambient pressure.



As shown in Figure 2a, before methylation, the carrier mobility of WGR was about 2000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with detailed calculation provided in the Supporting Information, suggesting the high quality of device. The resistance was about 6 k $\Omega$  and the Dirac point was at 16 V (Figure S1, Supporting Information), indicating the p-type doped nature resulted from the adsorption of water and oxygen molecules. As the reaction proceeded, the resistance of the device increased because the covalent modification broke the  $\pi$ - $\pi$  electron delocalization and thus decreased the electrical conductivity. Specifically, after 10-min reaction, the current on/off ratio of graphene was only about 10 with 10 mV bias voltage between drain and source  $(V_{\rm ds})$ , implying the existence of a graphene ribbon with large width (>10 nm).<sup>15,16</sup> Therefore, the uniform D band intensity in Figure 1d was not derived from the complete modification of the whole graphene sample but from the low spatial resolution of Raman technique. Thus, the ribbon width after 10-min reaction was in the range of 10-100 nm. After 30-min reaction. the on/off ratio remarkably increased, which further increased to about 10<sup>4</sup> after 40-min reaction, indicating that the on/off ratio as well as the bandgap of CGNRs could be conveniently tuned by controlling the reaction time. In addition, after the bandgap was opened, the current on/off ratio of CGNR was significantly affected by the reaction time. Reaction with a few more minutes could result in remarkable changes of transfer characteristics (Figure S2, Supporting Information) and current on/off ratios (Figure 2b). Therefore, the reaction time was crucial to tune the properties of the CGNR-based device, especially when the bandgap was opened.

Besides, this reaction was applicable for WGRs with larger widths, only by taking a longer reaction time (Figure 2b). High on/off ratios were obtained for all CGNR products whatever the width of starting material was. Therefore, the as-established chemical narrowing method based on the edge-selective reaction between graphene and DTBP had the potential to be a facile and universal approach for the development of CGNRs. It was unfortunate that the precise width of as-prepared CGNRs could not be easily measured using AFM because the height difference between pristine and methylated graphenes was indistinguishable. However, since GNRs with a width of  $\approx 6$  nm



**Figure 2.** a) The current  $(I_{ds})$  as a function of the gate voltage  $(V_{gate})$  for the CGNR-based device fabricated from WGR with 300-nm width and 3-µm length with different reaction time. b) Current  $I_{on}/I_{off}$  ratios as a function of reaction time for CGNR-based devices fabricated from WGRs with different widths.

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**Figure 3.** a) Transfer characteristics  $(I_{ds}-V_{gate})$  under various bias voltage  $(V_{ds})$  for the CGNRbased device fabricated from WGR with 300-nm width and 3-µm length after 30-min reaction. b)  $I_{ds}-V_{ds}$  characteristics for the device in (a) under various  $V_{eate}$ .

exhibited an on/off ratio of  $\approx 100$ ,<sup>[14–16]</sup> it was reasonable to estimate that the width of our CGNRs with such a high on/off ratio was well in the sub-10 nm range. Moreover, the relationship between the width of WGR and the photoinduced methylation time could be roughly formulated based on Figure 2b. To obtain a current on/off ratio of 100, it took 25 min, 30 min, 35 min and 40 min for WGRs with widths of 300 nm, 500 nm, 700 nm and 1 mm, respectively. Approximately, 5 more minutes were needed for an additional 200-nm width, indicating

the narrowing rate of the width from each edge was about 20 nm min<sup>-1</sup>. Assuming that the width of conduction channel in CGNRs with 100 on/off ratio was 10 nm, the relationship between the width of conduction channel ( $W_C$ ), the width of WGR ( $W_W$ ) and the reaction time (*t*) could be described by the equation:  $W_C = W_W - 20 \times 2(t - t_0)$ , where  $t_0$  ( $\approx$ 17.7 min) was the relaxation time, which might be caused by the activation and the slower rate at the beginning of the reaction. Based on this equation, the photoinduced methylation time could be roughly predicted.

To demonstrate the potential of our CGNRs in the application of electronics, we investigated the transfer characteristics of CGNRbased three-terminal device prepared from WGR with 300-nm width and 3-µm length. The *p*-type semiconducting feature was observed in the electrical transport measurement results (Figure 3). For relatively low  $V_{ds}$ , high on/off ratios were observed, i.e., 200 when  $V_{ds} = 10 \text{ mV}$  and 50 when  $V_{ds} = 100 \text{ mV}$ , suggesting the bandgap of CGNRs was larger than 100 meV.<sup>[17]</sup> Yet, when  $V_{ds}$  further increased, to a value larger than the bandgap, the electron transport would be caused by hopping rather than the semiconducting feature.<sup>[17]</sup> The on/off ratio significantly dropped to 10 when  $V_{ds} = 500 \text{ mV}$  and 2 when  $V_{ds} = 1 \text{ V}$ , respectively, suggesting that the bandgap of the device was in the range of 100-500 meV.<sup>[17]</sup>

To further investigate the electrical properties of CGNRs, variable-temperature electrical measurements were carried out in the vacuum chamber ( $\approx 10^{-5}$  Torr). CGNRbased device was fabricated from WGR with 500-nm width and 3-µm length after 40-min reaction. Figure 4a showed the relationship between the current  $(I_{ds})$  and the gate voltage  $(V_{gate})$  at different temperatures. As the temperature went down, the on/off ratio increased from 400 at room temperature to 5000 at 197 K and 10<sup>5</sup> at 97 K, respectively. More peaks were observed in the plot at 97 K, indicating the presence of quantized energy levels in the bandgap of CGNRs.<sup>[37,39]</sup> The resistance increased from  $10^7 \Omega$  at 297 K to  $10^9 \Omega$  at 97 K (Figure 4b), suggesting the

semiconductor behavior of CGNRs. The linear response of log(R) to 1/T at high temperature (200 to 300 K) in Figure 4c confirmed the semiconducting characteristic since semiconductors complied with the exponential dependence of *R* on *T*, i.e.,  $R \propto \exp(-\Delta/2k_{\rm B}T)$ ;<sup>[9,40]</sup> and a value of bandgap ( $\Delta = 120 \text{ meV}$ ) was extracted from the linear fitting result. The linear response of log(*R*) on  $1/T^{-1/3}$  (Figure 4d) indicated that the electron transport of graphene went through the variable range hopping (VRH) process, which might be resulted from the non-uniform modification of graphene.<sup>[9,40]</sup>



**Figure 4.** a)  $I_{ds}-V_{gate}$  characteristics at different temperatures for the CGNR-based device fabricated from WGR with 500-nm width and 3-µm length after 40-min reaction. b)  $I_{ds}-V_{ds}$  characteristics for the device in (a) under various temperatures. The resistance *R* as a function of c) 1/T and d)  $T^{-1/3}$  for the device in (a).

Mabrials Views

In summary, we elaborated an effective approach to fabricating CGNRs , a new type of quantum-confinement graphene nanostructure having tunable electrical conduction channels and bandgaps. Such kind of semiconducting nanoribbons was achieved by chemically narrowing the graphene conduction channels based on the edge-selective covalent reaction between graphene and DTBP molecules. The transport measurements proved that CGNRs behaved as semiconductors with tunable on/off ratios ranging from a few hundreds to  $\approx 10^4$ , much higher than that obtained from the conventional top-down etching techniques. The present approach may extend the potential of CGNRs to be an alternative material in the development of high-performance electronic devices.

## **Supporting Information**

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

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