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Micropatterning and Functionalization of Single Layer Graphene: Tuning Its Electron Transport Properties

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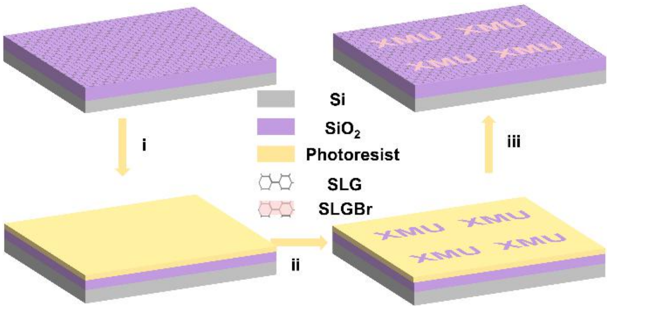
Abstract: As a promising 2D material, graphene exhibits excellent physical properties including single-atom-scale thickness and remarkably high charge carrier mobility. However, its semi-metallic nature with a zero bandgap poses challenges for its application in high-performance field-effect transistors (FETs). In order to overcome these limitations, various approaches have been explored to modulate graphene's bandgap, including nanoscale confinement, external field induction, doping, and chemical micropatterning. Nevertheless, the stability and controllability still need to be improved. In this study, we propose a feasible method that combines electrochemical bromination and photolithography to precisely tune the electron transport properties of single layer graphene (SLG). Through this method, we successfully fabricated various brominated SLG (SLGBr) micropatterns with high accuracy. Futher investigation revealed that the electron transport properties of SLG can be conveniently tuned by controlling the degree of bromination. The SLGBr exhibited a resistance, and have a decreasing conductance with the bromination degree increasing. When the bromination degree increased to a critical value, the SLGBr demonstrated semiconducting characteristics. This research offers a prospective route for the fabrication of graphene-based devices, providing potential applications in the realm of microelectronics.

Graphene has been considered as the most prospective material because of its excellent properties, including single-atom-scale thickness[1], extremely high charge carrier mobility[2], superior optical transparency[3], high thermal conductivity[4], etc.. Recently, the mass production of high-quality single layer graphene (SLG) at wafer scale makes it qualified in various possible applications such as micro/nano-electronics, sensors and actuators, microelectromechanical system (MEMS), etc.[5-7]. To this, the localized micropatterning and functionalization of SLG at wafer scale is crucial in order to tune the physical and chemical properties, e.g., band gap, electron conductivity, transmittance, wettability, etc., and to fulfil the requirements of various industrial domains[8].

Great efforts have been made to fabricate SLG patterns. Physical methods can be classified into top-down and bottom-up categories[9]. The top-down methods are to remove the carbon atoms from pristine SLG wafer by the energy-beam techniques including the focused laser beam, electron beam, plasma beam, reactive ion beam, etc.[10]. The top-down methods can be realized by either direct writing or template forming combined with various lithography techniques. The bottom-up methods are to synthesize specially sized SLG on the patterned catalysts such as copper, nickel, platinum, gold, etc.[11-13]. The most advantage of physical methods lies that the crystalline structure of SLG are not destroyed. Consequently, the intrinsic properties of SLG are kept very well. Nevertheless, the physical properties of SLG, e.g., the band gap, can be regulated by the external physical field[14]. However, when the external physical field were dismissed, the band gap of SLG would go back to zero.

Comparing physic methods, chemical micropatterning can change the crystalline structure and thus, change the physical and chemical properties of SLG[8]. Chemical adsorption[15] or doping[16] have been adopted to tune the SLG's properties by introducing the sp^3-C defects. However, after thermal annealing, many of the functionalized SLG materials change back to be pristine due to the weak interaction between SLG and the adsorbates or dopants, e.g., van der Waals' force[17], adsorption bond[18], or even chemical bond[19]. To this, we developed an in-situ electrochemically induced radical addition reaction to functionalize SLG with high efficiency and stability[20, 21]. Here we report that the functionalized SLG micropatterns has tuneable electron transport properties, making SLG act as single-atomic-thickness resistor or rectifier, depending on the introduced sp^3-C defects density.

The electrochemical micropatterning and functionalization procedures of SLG are depicted as in Scheme 1. First, a thin-layer viscosifier (HMDS) was spin-



Scheme 1 Preparing processes of brominated SLG with patterns. (i) photoresist coating, (ii) Photolithography, (iii) electrochemical brominating.

coated on the SLG wafer to increase the adhesion between SLG and photoresist. Second, a thin layer of photoresist (AZ5214E) film was spin-coated on the substrate. Then, the photoresist film was exposed by the laser-beam direct-writing photolithography. Later on, the exposed photoresist was removed by tetramethylammonium hydroxide for several times and the aimed SLG micropattern array was obtained. After that, the obtained SLG micropattern array was immersed in an aqueous electrolyte containing 10 mM KBr and 10 mM H_2SO_4 to performed bromination addition reaction by cyclic voltammetry in a potential range from -0.75 to 1.2 V vs. Hg/Hg_2SO_4 reference electrode with a scan rate of 100 mV/s for certain cycles (See Figure S1). Finally, the brominated SLG (SLGBr) micropatterns were obtained after removing the photoresist protection layer by rinsing with acetone and isopropanol.

As reported very recently by us, the functionalization of SLG is realized by the bromination addition reaction[20]. Because SLG is conductive enough to act as the working electrode, bromide anions are oxidized to bromine radicals, which can react with SLG to form SLGBr. When SLG changes into SLGBr, the interfacial electrochemical reaction activity will be decreased because the Faraday current keeping decreasing with the potential scanning going on. The SLGBr micropatterns "XMU", the acronym of Xiamen University, were observed to have a different colour with SLG by optical microscopy (Figure 1a). The corresponding images of scanning electron microscopy (SEM) and scanning Raman microscopy (SRM) were shown in Figure 1b and 1c. The clear boundaries between the SLG and SLGBr were also observed, indicating the different properties between them.

The Raman spectrum of the SLGBr region is much different from that of the SLG region (Figure 1d). The pristine SLG has a G-peak at near 1586 cm^{-1} and a 2D peak at 2687 cm^{-1}. The 2D-peak is sharp and symmetrical, and the peak intensity is about 4 times larger than that of G-peak, indicating that the pristine SLG has a perfect lattice structure[22]. After the functionalization by bromination addition reaction, the newly observed D-peak (~1350 cm^{-1}) and D'-peak (~1620 cm^{-1}) represents the sp^3-C defects[23], indicating that the symmetry of the lattice is changed due to the formation of C-Br bond. Furthermore, the G-peak blue-shifted to 1597 cm^{-1} at the brominated region, and 2D peak blue-shifted to 2692 cm^{-1}, predicting that SLGBr is p-type doping[24], which is consistent with the strong electron absorption ability of bromine.

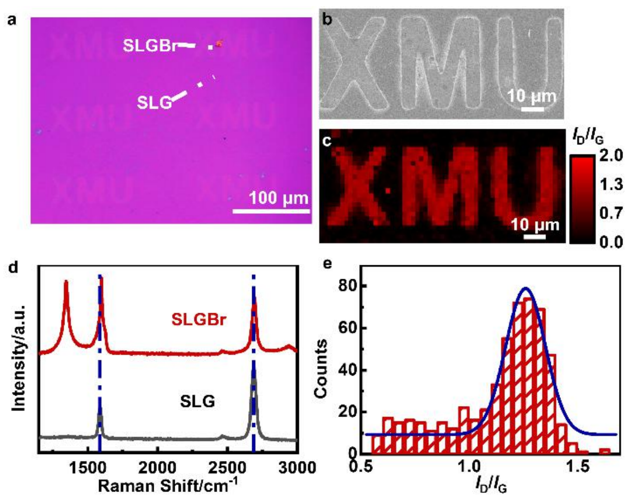


Figure 1 The optical image (a) and SEM image (b) of patterned SLGBr with the "XMU" logo.(c) Raman I_D/I_G mapping of the patterned SLGBr. (d) The corresponding Raman spectra of pristine SLG and SLGBr. (e) Statistical I_D/I_G histograms from the mapping image of (c).

The intensity ratio (I_D/I_G) is usually adopted to characterize the defect density of graphene, that is, the ratio of the sp^3 to sp^2 bonding character. A higher the I_D/I_G ratio means a higher defect density[25]. The statistical analysis of SRM image gives a distribution of I_D/I_G ratio as shown in Figure 1c. The I_D/I_G ratio in the "XMU" region is much higher than that in the remaining region, which indicates that photoresist micropattern can protect well the underlying graphene and let the bromination addition reaction selectively occur in the exposed area. The statistical I_D/I_G-ratio histogram was employed to analyzed the bromination degree of SLG. From Figure 1e, I_D/I_G ranged from 0.5 to 1.5 with a mid-value about 1.2, suggesting that the bromination degree of SLGBr micropattern was pretty uniform.

To demonstrate the versatility and reliability of the method, SLGBr micropattern array such as square ring, cross and an H- type Chinese knot were fabricated. The optical microscopy images of the SLG micropatterns after laser-beam direct-writing photolithography were shown in Figure 2a-2c, and the relevant optical images of the SLGBr micropatterns were shown in Figure. S2, indicating the clear SLG/SLGBr boundaries. The relevant I_D/I_G distribution of the SLGBr micropatterned SLG was characterized by the SRM as shown in Figure 2d-2f, indicating the uniform functionalization of bromination addition reaction.

We have demonstrated that the electron transport (i.e., electronic properties) and interfacial electron transfer (i.e., electrochemical properties) of functionalized SLG will change a lot from the pristine SLG[20]. To investigate the electron transport properties of SLGBr, we designed and fabricated the SLG-SLGBr interdigitated electrodes with a pair of Cr/Au belts as the current collectors (Scheme 2) to construct a field-effect transistor (FET), where the SLG electrode acts as the drain, the SLGBr acts as the source, and the Si/SiO_2 substrate acts as the gate. In order to investigate the characteristics of the devices, SLG electrodes and SLGBr electrodes were prepared simultaneously. The SLG electrodes exhibit resistance characteristics and p doping due to the residual photoresist (Figure S 3a-3b), while the SLGBr electrodes with higher defect density showed semiconducting characteristics (Figure S 3c-3d). Akin to chemical functionalization, electrochemically induced bromination addition introduced new sp^3 C-Br bond to SLG. Because of the asymmetric broken honeycomb structure, the bandgap of SLGBr rises, and a semimetal–semiconductor transition takes place in SLGBr.

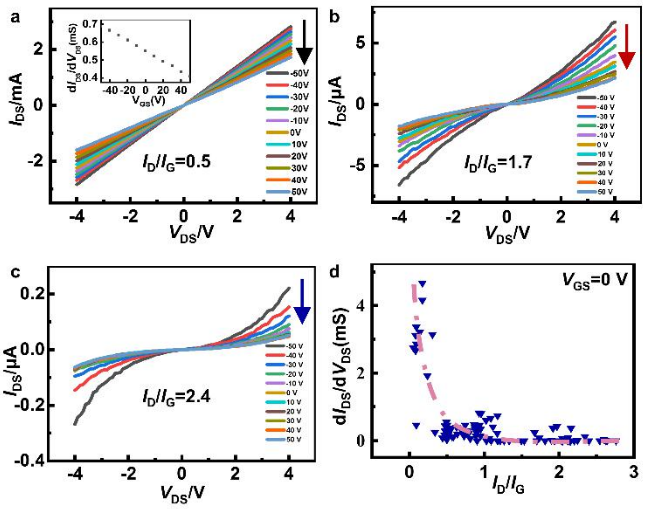


Figure 3 (a-c) The I_{DS}-V_{DS} curves of the SLGBr Interdigitated Electrode when I_D/I_G value is 0.5, 1.7 and 2.4, respectively. Inset: the slope of the I_{DS}-V_{DS} curves changes with V_{GS}. (d) The statistic relationship curve between the bromination degree (I_D/I_G) and the conductance (dI_{DS}/dV_{DS}) at V_{GS}=0 V.

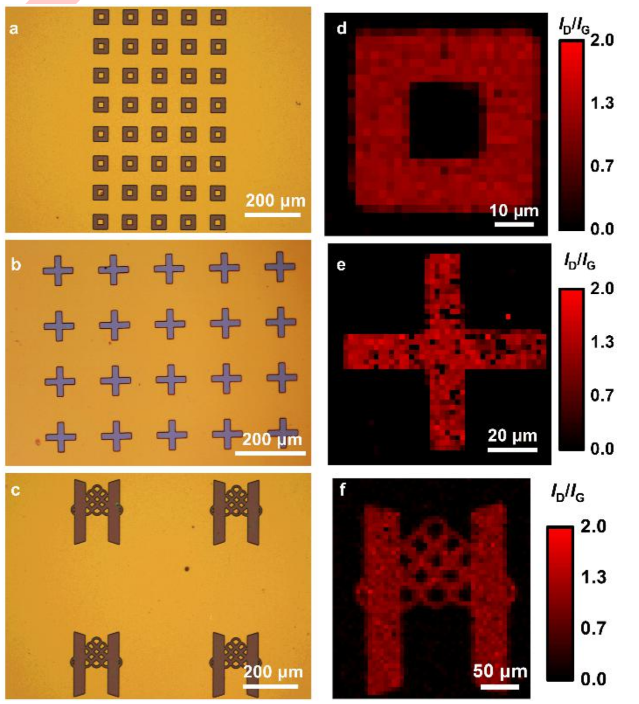
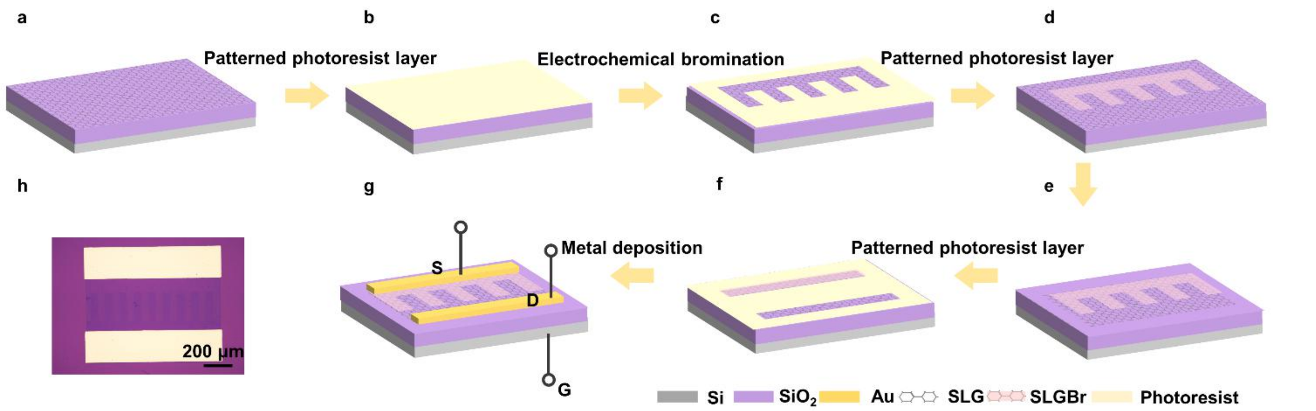


Figure 2 (a-c) Optical images of SLG with photoresist patterns, including (a) square rings, (b) crosses and (c) H- type Chinese knot. (d-f) Corresponding Raman I_D/I_G mapping of the SLGBr patterns.



Scheme 2 (a-g) Preparing processes of the graphene Interdigitated Electrodes with designed SLGBr patterns. (h) The optical image of a typical Interdigitated Electrode with patterned SLGBr.

Figure 3a-3c show the I_{DS}-V_{DS} curves of the SLGBr/SLG FET with different bromination degree characterized by the statistical I_D/I_G mid-values from the SRM images of SLGBr. With the low bromination degree (I_D/I_G: 0.5 in Figure 3a), the I_{DS}-V_{DS} curves shows a typical electronic property of a resistor. The conductance, i.e., the slope of the I_{DS}-V_{DS} curves changes linearly with V_{GS} in a potential region [-50 V, +50 V], shown as the insert of Figure 3a. The voltage-sensitive feature demonstrates the potential application of SLG into micro-varistor. With the higher bromination degree (I_D/I_G: 1.7 in Figure 3b or 2.4 in Figure 3c), the I_{DS}-V_{DS} curves were obviously different from those in Figure 3a, presenting the characteristics of current rectification. The results show that the SLGBr will be changed into a semiconductor if the bromination degree becomes higher[20, 26]. This result is similar to our previous study, but due to the low degree of bromination, the semiconductor characteristics are less significant than before[23]. We performed the electronic measurements of the FETs with different bromination degree and different V_{GS} bias, and the statistic relationship between the conductance (dI_{DS}/dV_{DS}) and the bromination degree (I_D/I_G) is shown in Figure 3d. The critical I_D/I_G value between conductor and semiconductor can be estimated as 0.6. The mechanisms of the change of electron transport properties needs to be further studied in future.

In conclusion, laser beam direct-writing photolithography and electrochemically induced bromination addition reaction were adopted for the micropatterning and functionalization of SLG. We found that the brominating functionalization can tune the electron transport properties of SLG by controlling its bromination degree. The conductance of SLGBr keeps decreasing at low bromination degree. After a critical value, SLGBr will become a semiconductor. This work demonstrates the possibility for the fabrication of ultrathin microelectronic devices by SLG.

Supporting Information

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate.))

Acknowledgements

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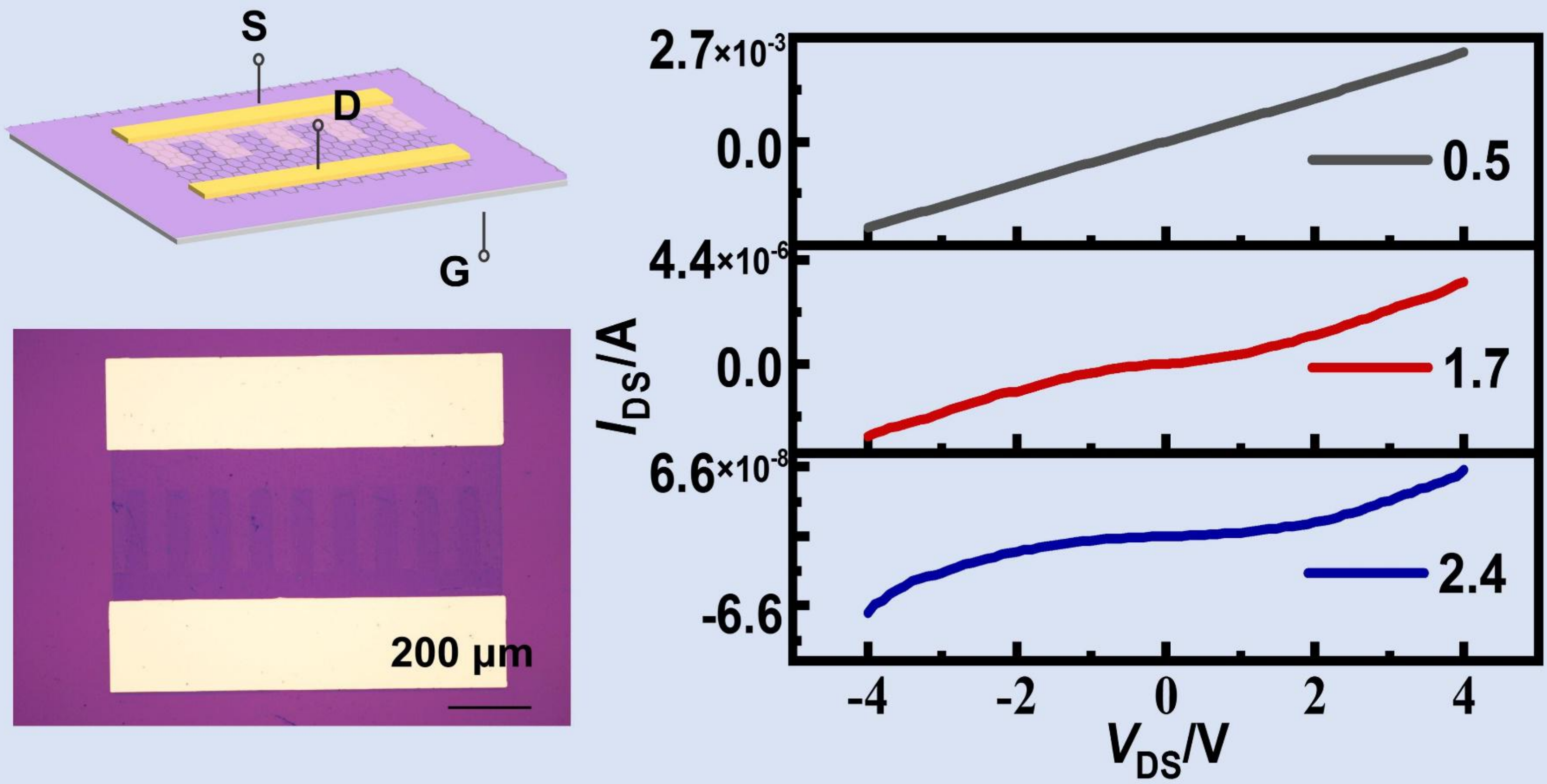

单层石墨烯微米尺度图案化和功能化：调控电子传输特性

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摘要：石墨烯具有优异的物理特性，如单原子厚度、极高的载流子迁移率等。然而，其零带隙的半金属特性限制了题在高性能场效应晶体管中的应用。为此，研究者们提出了石墨烯纳米化、外场诱导、掺杂以及化学图案化等策略，以调控其带隙宽度。但是，这些方法的可控性以及稳定性还需要进一步改善。在本研究中，我们提出采用电化学溴化并结合光刻图案化调控单层石墨烯的电子传输特性。通过这种方法，我们成功制备了图案化的溴化石墨烯（SLGBr）。进一步研究表明单层石墨烯的电子传输性能可以通过溴化程度来调控。当溴化程度较小时，SLGBr 表现为电阻特性，且其电导随溴化程度增加而减小；当溴化程度增加到一定值时，SLGBr 表现为与半导体类似的特性。本研究将为全石墨烯器件的制备提供可行的技术路线，拓展其在微电子领域的应用。

关键词：石墨烯图案化；电子传输；电化学溴化；光刻；全石墨烯器件