Atomic Dopants Involved in the Structural Evolution of Thermally Graphitized Graphene

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Abstract: Thermally doped nitrogen atoms on the sp²-carbon network of reduced graphene oxide (rGO) enhance its electrical conductivity. Atomic structural information of thermally annealed graphene oxide (GO) provides an understanding on how the heteroatomic doping could affect electronic property of rGO. Herein, the spectroscopic and microscopic variations during thermal graphitization from 573 to 1373 K are reported in two different rGO sheets, prepared by thermal annealing of GO (rGOtherm) and post-thermal annealing of chemically nitrogen-doped rGO (post-therm-rGON2H4).

The spectroscopic transitions of rGO_N2H4 in thermal annealing ultimately showed new oxygen-functional groups, such as cyclic edge ethers and new graphitized nitrogen atoms at 1373 K. During the graphitization process, the microscopic evolution resolved by scanning tunneling microscopy (STM) produced more wrinkled surface morphology with graphitized nanocrystalline domains due to atomic doping of nitrogen on a post-therm-rGON2H4 sheet. As a result, the post-therm-rGON2H4-containing nitrogen showed a less defected sp²-carbon network, resulting in enhanced conductivity, whereas the rGOtherm sheet containing no nitrogen had large topological defects on the basal plane of the sp²-carbon network. Thus, our investigation of the structural evolution of original wrinkles on a GO sheet incorporated into the graphitized N-doped rGO helps to explain how the atomic doping can enhance the electrical conductivity.

Keywords: doping · graphene · Raman spectroscopy · scanning tunneling microscopy · thermal annealing

Introduction

Atomically flattened graphene that consists of a single layer of pure sp²-hybridized carbon atoms has attracted attention due to its remarkable electronic properties and possible applications in various fields, such as optoelectronics,[11] sensors,[12] and organic electronics.[13] There are several ways to synthesize graphene, such as the mechanical cleavage of graphite,[4] epitaxial growth on silicon carbide,[5] chemical vapor deposition (CVD) of hydrocarbons on transition-metal surfaces,[6] and chemical/thermal reduction/annealing of graphene oxide (GO).[7–10] For realistic applications of graphene as post-silicon alternatives, processes must be manageable and suitable for mass production. Thus, chemical or thermal routes of graphene synthesis have been developed,[1,7–9] and those methods are potentially applicable to all types of samples, such as papers, powders, and films.[1,11–12] Numerous applications of chemically or thermally reduced graphene oxide (rGO) have been reported in the field of rGO-based electronics.[13–14] The electronic properties of rGO are strongly associated with the distribution of sp²-carbon clusters.[1,3,15] According to the degree of reduction, the electronic properties of rGO vary from insulator (e.g., GO) to semiconductor and semimetal. Transport of the charge carriers in the rGO sheet is limited by vacancies in the sp²-carbon network.[1,16–17] To achieve a high conductivity of rGO, a structure with more sp² than sp³ carbons is required.

In particular, thermal annealing (or thermal graphitization) of rGO at high temperature has been shown to significantly recover sp²-carbon networks, giving better conductivity than chemically or thermally reduced GOs at low temperature.[18] The conductivity of thermally annealed rGO increased about four orders of magnitude over the value of the original GO, but is less than two orders of magnitude smaller than the value of the pristine graphene.[19] This is due to the different electron transport across the inhomogeneous basal plane on rGO in comparison with the homogeneous basal plane on graphene.[19–20] The inhomogeneity can be attributed to the changes in atomic structure due to removal of oxygen atoms and rearrangement of carbon atoms during conversion from GO to rGO, which can strongly affect the electronic and mechanical properties of rGO. Therefore, it is critically important to understand the struc-

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tural information of the single rGO, including the carbon–carbon connectivity, to achieve an increase in the electrical conductivity of the rGO film. To date, the local structural properties of the single GO or rGO sheet during the reduction process have been less frequently reported than the bulk properties of GO or rGO films or powders.\cite{20-21}

Generally, a structural change in the size of sp²-carbon clusters in a network of sp² and sp³ carbon can be assessed by Raman spectroscopy. It is expected that the Raman signals provide the sizes of sp²-carbon clusters and the defect or vacancy density.\cite{18,22} Recently, FTIR spectroscopy detected unique IR absorption on the rGO due to structural changes on the edge of the rGO sheet.\cite{19,23} On the other hand, microscopic investigations, such as high-resolution transmission electron microscopy (HRTEM)\cite{21} and scanning tunneling microscopy (STM)\cite{20} revealed topological images of rGO in the atomic scale. However, results of those measurements were not sufficiently clear to fully explain the atomic structure of the rGO even though those measurements were obtained by using the most advanced technology available at that time. Therefore, a reasonable and accurate investigation regarding the atomic structures as well as the chemical functionality of thermally annealed rGO sheets is required for future fundamental research and further applications. In addition, the inhomogeneity in the chemical compositions of rGOs due to atomic dopants, such as oxygen or nitrogen, can influence the graphitization process, which can then result in the rearrangement of the carbon atoms. Thus, a microscopic investigation in the real atomic scale is required to understand the electrical properties of rGOs associated with the effects of heteroatom dopants. Unfortunately, atomic structural changes of the rGO monolayers during thermal graphitization (e.g., >1000 K) have not yet been reported.

Herein, real scale atomic structures and topological changes are reported in a single rGO sheet by using STM after thermal graphitization at high temperatures from 573 K to 1373 K, which were confirmed by spectroscopic investigations using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and FTIR spectroscopy. Two different thermally reduced GOs at high temperature, direct thermal reduction/annealing of GO (rGOtherm) and post-thermal annealing of chemically reduced GO (post-therm-rGO)\cite{23} were introduced and carefully studied for atomic structural evolution in thermal graphitization. The former should have only carbon backbones containing no nitrogen, whereas the latter should have carbon backbones containing nitrogen. We suggest that the surface morphology of carbon backbones of rGOs is verified by chemical or physical processes in atomic structures and that the enhancement in the electrical conductivity of post-therm-rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} is originated from the N-doped sp²-carbon network.

Results and Discussion

Scheme I depicts the proposed structural evolution of GO during different thermal graphitization processes (routes I and II). It was expected that the structural evolution during thermal graphitization of rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} containing nitrogen and oxygen atoms would be different from GO containing no nitrogen. The oxygen atoms on the rGO\textsubscript{therm} sheet were expected to be able to thermally diffuse over the surface without interruption of nitrogen atoms. On the other hand, the nitrogen atoms of post-therm-rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} were expected to cause the oxygen groups to thermally diffuse in the limited local regions, leading to fewer defects and more wrinkled morphology. Also, the dopant effect of the electron-rich nitrogen atom could be the source of the higher conductivity of nitrogen-doped rGO than that of the rGO containing no nitrogen.\cite{24} In this study, after thermal annealing at 1373 K, the conductivity of the post-therm-rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} film was measured by approximately 30000 Sm\textsuperscript{-1}, which was two times larger than that of the rGO\textsubscript{therm} film containing no nitrogen (ca. 15000 Sm\textsuperscript{-1}).

To aim the understanding of the structural evolution during a thermal graphitization of rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} (route I, Scheme I), morphological changes from GO to rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} and to post-therm-rGO\textsubscript{N\textsubscript{2}H\textsubscript{4}} at each temperature were observed by STM. Figure 1a shows an STM image of an as-made GO sheet on highly oriented pyrolytic graphite (HOPG). In general, the STM apparent height represents the physical height of materials (or molecules) on the surface and its tunneling probability. Thus, a topographical fluctuation of 2.0 nm (in a
scale from black to white) indicates conductivity fluctuation on the GO surface, which is induced by many nonconductive oxygen-functional groups, such as hydroxyl (C–OH), carboxyl (C(O)OH), carbonyl (C=O), epoxy (C–O–C), and ether (C–O) groups. At the positive bias on the sample, electrons from the tip can tunnel into unoccupied molecular orbitals (LUMO) of GO. Thus, such high fluctuations in the STM apparent height of the GO image indicate a lower conductivity of the LUMO of GO compared with that in HOPG. On the other hand, as-reduced rGO N2H4 sheets showed less surface roughness than as-made GO, which was measured as approximately 1.2 nm from the HOPG surface (Figure 1b). Furthermore, the irregular, globular wrinkles on the as-made GO were flattened into regularly aligned discs on the as-reduced rGO N2H4, which are anticipated results due to the restoration of sp²-carbon atoms (two-dimensional features) from sp³-carbon atoms of the oxygen-functional groups (three-dimensional features).

Post-thermal annealing of as-reduced rGO N2H₄ proceeded at high temperature from 573 K to 1373 K under a reductive atmosphere (e.g., H₂/Ar). Figure 1c–e show the typical STM images at critical temperature. At 773 K, terrace-like (or rippled) folded features were observed as marked with the red-dotted lines (ca. 25 nm wide, as shown in the line profile of Figure 1c). When the temperature increased to 973 K (Figure 1d), the terrace-like features contained flat domains with a step of about 0.4 nm height, in which the domain boundary is marked by a red-dotted line. Furthermore, in atomic resolution images, crystalline domains are clearly observed (Figure 1e). From the cross-sectional analysis of the crystalline domains (Figure 1f, also see Figure S1 in the Supporting Information), a hexagonal pattern of the single rGO sheet/HOPG was obtained, indicating AB-staked graphite sheets. The distance between the nearest neighboring atoms in the domains was approximately 2.5 Å on the post-thermally annealed rGO N2H₄ sheet (Figure 1f), similar with approximately 2.7 Å in the crystalline lattice on HOPG (Figure 1g). Eventually, post-thermal annealing of the rGO N2H₄ sheet at 1373 K led to the formation of white protrusions on atomically flat rGO N2H₄ sheets (Figure 2a). In atomic resolution images, the graphitized lattice was clearly observed on a single rGO N2H₄ sheet (Figure 2b). Also, the white protrusions were imaged at the atomic level, showing crystalline domains (as marked with red-dotted lines in Figure 2c and d). Interestingly, crys-
talline patches (or islands) rather than lattice defects, thicknesses of which were measured as approximately 0.3 nm of the single-graphene layer thickness, were predominantly observed (Figure 2d).

The thermal-annealing process of GO should involve the removal of oxygen groups, such as CO/CO$_2$ or the modification of adjacent carbon atoms (including sp$^2$-hybridized carbon) into other oxygen-functional groups [26]. Thus, thermal-annealing-induced topological changes should be attributed to the numbers and locations of the oxygen-functional groups on the rGO surfaces. Unlike rGO$_{N_2H_4}$, rGO$_{therm}$ did not contain nitrogen-functional groups that produced differences in atomic structures after thermal annealing (route II in Scheme 1). In Figure 3, terrace-like features (as marked with red-dotted lines) appeared irregularly at 973 K (Figure 3a), became smooth at 1373 K (Figure 3b), and topological defects (with the carbon atomic height marked with red lines) appeared in the well-graphitized sp$^2$-carbon network (Figure 3d). The hexagonal pattern of the AB-staked graphite sheet was clearly observed and was comparable with that of post-therm-rGO N$_2$H$_4$. However, no graphene-like patches appeared, in contrast to the post-therm-rGO N$_2$H$_4$. Furthermore, thermal graphitization on GO should be controlled by the diffusion rate of oxygen atoms. If the diffusion of oxygen atoms occurs slowly and the structural defects are not sufficiently recovered, the removal of the oxygen atoms in CO/CO$_2$ can easily produce defects. As a result, many defected rGO$_{therm}$ sheets were observed when the thermal annealing was conducted rapidly from room temperature to 1373 K for a short time (within 30 seconds; Figure S2 in the Supporting Information). Therefore, it is believed that the diffused rearrangement of oxygen atoms can determine the surface morphology. In addition, the thermal graphitization of rGO can be limited in recrystallization into the optimum hexagonal configuration with a large size because of a thermodynamic diffusion barrier (e.g., defects or nitrogen atoms) of oxygen atoms, even for a slow thermal heating from room temperature to 1373 K.

For a deeper understanding of these structural changes in the rGO$_{N_2H_4}$ sheet, chemical characterizations, such as XPS, Raman spectroscopy, and FTIR spectroscopy, were performed according to thermal-annealing temperature. Figure 4 shows the carbon (C1s) XPS spectra at each step.

![Figure 3](image3.png)

**Figure 3.** STM images of direct thermally annealed rGO$_{therm}$ sheets on HOPG at a) 973 K and b)–d) 1373 K. Image size: a) 70 × 70 nm$^2$, b) 73 × 73 nm$^2$, c) 20 × 20 nm$^2$, and d) 10 × 10 nm$^2$. Imaging conditions: tunneling current a), b) $I = 100$ pA, c) $I = 400$ pA, and d) $I = 800$ pA; sample bias a), b) $V = 400$ mV, c) $V = 100$ mV, and d) $V = 70$ mV. The thermal treatment of the samples was heated to each temperature within 90 seconds.

![Figure 4](image4.png)

**Figure 4.** C1s XPS spectra of a) post-thermally annealed rGO$_{N_2H_4}$, as-reduced rGO$_{N_2H_4}$, and as-made GO; b) direct thermally annealed rGO$_{therm}$ and as-made GO; c), d) N1s XPS spectra of post-thermally annealed rGO$_{N_2H_4}$.

The deconvoluted peaks of the C1s spectra were assigned to the oxygen-functional (Figure 4a) and nitrogen-functional groups (Figure 4b). In the direct thermal reduction/annealing process, the oxygen-functional groups on rGO$_{therm}$ were drastically decreased at 573 K and gradually decreased as temperature increased to 1373 K. On the other hand, despite post-thermal annealing of rGO$_{N_2H_4}$ at high temperature, such as the C1s spectra, were not significantly changed by temperature. The C=N peak was fixedly observed at all temperatures (Figure 4b), whereas the C=O peak was gradually decreased, when temperature increased (Figure 4a). The C=N peak in the C1s spectra was confirmed by the N1s spectra on post-therm-rGO$_{N_2H_4}$ (Figure 4c and d), which indicated the existence of nitrogen-functional groups [24, 27] (e.g., C−N and C=N bonds). It was also believed that the C=N peak ob-
served at 285.8 eV was overlapped with the C–O peak in the Cl s spectra of the rGO_{N2H4} (Figure 4b). The N1 s spectra of post-therm-rGO_{N2H4} in Figure 4c and d represent the C=N bonding energies of the tertiary (e.g., pyrrolic or pyridinic types) and quaternary N atoms (e.g., a graphitic type), whereas N1 s of rGO_{thrm} was not detected.

These variations in the oxygen-functional groups on GO and rGos should lead to changes in the vibrations of sp² carbon in Raman spectra (Figure 5a and b), corresponding to the first-order D and G bands and the second-order 2D and as-made GO and b) post-thermally annealed rGO N2H4 and as-reduced rGO_{N2H4}; c),d) FTIR spectra of (a) and (b) samples, respectively.

Figure 5. a),b) Raman spectra of a) direct thermally annealed rGO_{thrm} and as-made GO and b) post-thermally annealed rGO_{N2H4} and as-reduced rGO_{N2H4}; c),d) FTIR spectra of (a) and (b) samples, respectively.

to the first-order D and G bands and the second-order 2D band at approximately \( \bar{\nu} = 1350, 1600, \) and 2700 cm⁻¹, respectively.[22] During thermal graphitization through route II, the ratio of the intensity of the D to the G band of as-made GO (\( I_D/I_G = 0.85 \)) increased in the rGO_{thrm} sheet (\( I_D/I_G = 1.05 \)) at 1373 K, and the 2D band became distinguishable (Figure 5a). As shown in XPS data at high temperature, defunctionalization of oxygen groups on rGO_{thrm} was predominantly contributed to the increase of the \( I_D/I_G \) ratio in Raman spectra. Also, an increase in the \( I_D \) indicated an increase of physical defects at high temperature (e.g., 1373 K), as shown in the STM image (Figure 3c). On the other hand, the \( I_D/I_G \) increased in the as-reduced rGO_{N2H4} sheet (\( I_D/I_G = 1.04 \); Figure 5b). As was reported, chemical reduction normally resulted in a relative increase of the intensity of the D band.[20] However, when the temperature increased to 1373 K, the \( I_D/I_G \) ratio of post-therm-rGO_{N2H4} samples (\( I_D/I_G = 0.99 \)) was decreased. Furthermore, the 2D band of rGO_{N2H4} was obviously conspicuous after post-thermal annealing. These results suggested that regraphitization into the sp²-carbon network was very effective, which was not originated from the defunctionalization of oxygen groups that is consistent with no significant changes of the Cl s spectra in XPS data.

XPS and Raman spectra (Figures 4 and 5a and b, respectively) provided new insight into post-thermal annealing effects on the structural evolution from rGO_{N2H4} to graphene (a single layer of well-crystallized sp²-carbon network) in STM images (Figures 1 and 2). Graphitization on rGO_{N2H4} was obviously detected by Raman spectra (e.g., an increase in the peak intensity of the 2D band), as was revealed by atomic-resolution STM images. However, some functionalized groups in post-therm-rGO_{N2H4} were sustained at 1373 K, as shown in the XPS spectra (Figure 4b). These defects in the chemical structure of rGO_{N2H4} also appeared in Raman spectra (Figure 5b), even though thermal graphitization through route I proceeded successfully on the basal plane, as shown in the STM images at 1373 K (Figure 2). Consequently, the formation of crystalline domains (or patches) derived from terrace-like features can be explained by the existence of heterogeneous chemical structures on the basal plane of the rGO_{N2H4} sheet even after post-thermal annealing at very high temperature (Figures 1 and 2).

For the detailed characterization of chemical functionalities, FTIR spectra were recorded at each step of thermal annealing of GO and rGO_{N2H4} (Figure 5c and d, respectively). The oxygen-functional groups on the as-made GO were represented primarily by peaks according to the functionalities of hydroxyl (C–OH, broad peak at \( \bar{\nu} = 3050–3800 \) cm⁻¹), carboxyl/carbonyl (COOH/C=O at \( \bar{\nu} = 1650–1850 \) cm⁻¹), and epoxy/ether (C=O-C/O at \( \bar{\nu} = 1000–1250 \) cm⁻¹ as marked with a dotted grey box) groups. Many functionalized oxygen groups produced overlapped peaks in FTIR spectra.[15,23,26] In contrast with the as-made GO, as-reduced rGO_{N2H4} created the graphitized C=C bonds (i.e., the sp²-hybridized C–C in-plane stretching) that were assigned to peaks at \( \bar{\nu} = 1450–1600 \) cm⁻¹. In particular, three peculiar bands were observed in post-therm-rGO_{N2H4} and rGO_{thrm} at high temperature: 1) post-therm-rGO_{N2H4} showed a strong peak at approximately \( \bar{\nu} = 800–1000 \) cm⁻¹ corresponding to asymmetric C-O-C stretching,[15,23,26] This unique strong peak of post-therm-rGO_{N2H4} was assigned to the cyclic edge (-O-) groups (Figure 5d) [15,23,26]. Also, rGO_{thrm} (Figure 5c) produced a peak of (-O-) at \( \bar{\nu} < 1000 \) cm⁻¹ at 1373 K, but the intensity was weak. 2) a strong peak from the ether bonds (C=O) appeared at approximately \( \bar{\nu} = 1000–1150 \) cm⁻¹ for both rGO_{thrm} and post-therm-rGO_{N2H4} and had strong intensity with increasing temperature. This band was taken into account by the reformation of ether groups:[15,23,28] 3) the peak at \( \bar{\nu} = 1650–1750 \) cm⁻¹ appeared in rGO_{N2H4} and was sustained up to 1373 K, whereas the carboxyl/carbonyl groups (COOH/C=O at \( \bar{\nu} = 1650–1850 \) cm⁻¹) of rGO_{thrm} almost completely disappeared at 973 K. The peak at \( \bar{\nu} = 1650–1750 \) cm⁻¹ presumably originated from the C=3 bonds formed by reactions of adsorbed/inserted nitrogen atoms (from hydrazine).[19,20] Consequently, FTIR spectra revealed that, in addition to the desorption of the oxygen-functional groups at high temperatures, the oxygen-functional groups of C–O and (-O-) were reformed on both...
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rGO$_{therm}$ and post-therm-rGO$_{N2H4}$, and the C=N was newly formed on only post-therm-rGO$_{N2H4}$. Based on the chemical structural analysis of rGO$_{therm}$ and post-therm-rGO$_{N2H4}$, the thermal graphitization and the formation of chemical defects occurred at almost the same time.

Figure 6 shows a scenario scheme for the thermal annealing process (through routes I and II) accompanying topological changes on rGO$_{therm}$ and rGO$_{N2H4}$: 1) the oxygen-functional groups (e.g., C=O bonds are more stable than those of other oxygen-functional groups, such as thermally stable ether groups). The functional groups, such as thermally stable ether groups. The reduction reaction or removal of oxygen atoms could be terminated as topological defects in the atomic scale STM images can provide new insight for understanding of rGOS, especially for clear elucidation about the higher conductivity of the N-doped rGO in comparison with the rGO$_{therm}$ containing no nitrogen. Therefore, the atomic scale STM images can provide new insight for understanding of rGOS, especially for clear elucidation about the higher conductivity of the N-doped rGO in comparison with the rGO$_{therm}$ containing no nitrogen.

Conclusion

In summary, spectroscopic and microscopic analyses suggested that the thermal graphitization of both rGO$_{therm}$ and rGO$_{N2H4}$ sheets proceeded through the formation of the terrace-like domains derived by the reformation of oxygen-functional groups, such as thermally stable ether groups. The progress toward the thermally diffused rearrangement of oxygen atoms could be terminated as topological defects in the rGO$_{therm}$ sheets. However, the progress in the N-doped rGO$_{N2H4}$ sheets was limited by the formation of graphene-like crystalline patches, leading to a sp$^2$-carbon network with fewer defects, eventually resulting in higher conductivity than that of the rGO$_{therm}$ containing no nitrogen. Therefore, the atomic scale STM images can provide new insight for structural evolution of original wrinkles on GO sheets into graphitized rGO, which can lead to a deeper understanding of rGOS, especially for clear elucidation about the higher conductivity of the N-doped rGO in comparison with the rGO$_{therm}$ containing no nitrogen.

Experimental Section

Sample preparation: Water-dispersed single GO sheets were synthesized by the modified Hummers method according to a previous report. A single GO sheet on freshly peeled HOPG was used for STM (AFM/SPM 5100 system, Agilent) and was prepared through the spin casting of an aqueous suspension of the GO solution (0.14 mg mL$^{-1}$). For other surface characterizations, such as XPS (VG microtech ESCA 2000) and Raman spectroscopy (Renishaw, RM1000-Invia) measurements, GO films on Si or SiO$_2$ substrates were prepared by drop casting or spin casting of an aqueous suspension of the GO solution (0.5 mg mL$^{-1}$). For FTIR spectroscopy measurements (Bruker IFS-66/S), highly pressurized pellets of a 1:100 dry mixture of ground GO powder with KBr (Aldrich) were used.

Thermal annealing: All GO samples were dried in a vacuum oven at 353 K for 24 h. For the chemical reduction to rGO$_{N2H4}$, the GO samples were placed in a glass bottle under hydrizine vapor at 353–373 K for 24 h, thoroughly washed with deionized (DI) water, and then dried in a vacuum oven at 353 K for 24 h. The thermal reduction/annealing of the...
samples was performed by a programmed heating/cooling process under Ar containing 10% H₂ by a rapid thermal annealing (RTA) system (SAM Vac CS410, Eurotherm 2040 Temperature controller); it was initiat- ed at RT, rapidly heated to high temperature (e.g., 1373 K) within a few tens of seconds (30 or 90 seconds), and then slowly cooled to low temperature (e.g., 323 K) within 15 min.

Analyses: STM analysis was performed by a Pt/Ir tip in an environmental chamber under Ar gas. Raman spectroscopy measurements were performed at λ≈514 nm. The electrical conductivity of rGO pallets, prepared by thermal annealing at 1373 K, pressed from powder, and kept in a vacuum oven at 423 K, was measured by using a Hall effect measurement system (HMS-3000, ECOPiA) at RT.

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