Synthesis and characterization of potassium-doped multilayer graphene prepared by wet process using potassium hydroxide

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Abstract

Potassium (K) doping of multilayer graphene was demonstrated by means of a wet chemical process using potassium hydroxide (KOH) aqueous solution (KOH treatment). The presence of K atoms along the stacking direction was confirmed from depth profiles of \(^{41}\)K\textsuperscript{+} ions obtained by time-of-flight secondary ion mass spectroscopy (TOF-SIMS). The intensity images of \(^{41}\)K\textsuperscript{+} ions obtained by TOF-SIMS suggested that the K atoms existed throughout the whole area. For the KOH-treated multilayer graphene, no peak due to K intercalation between graphene layers was obtained by x-ray diffraction (XRD); in Raman spectra, splitting of the G-band peak and disappearance of the 2D-band peak were not observed. A graphite intercalation compound structure was not determined by either XRD or Raman results. However, the up-shift in the G-band peak position in the Raman spectra suggested that K atoms were doped in the graphene. X-ray photoelectron spectroscopy carbon 1s spectra implied that KOH treatment resulted in K-termination at the edges and/or domains of graphene. In addition, a Cls shoulder peak appeared at 1 eV higher binding energy compared to the Cls peak of pristine graphene. Temperature-dependent conductivity measurement results indicated that the conductivity of multilayer graphene was increased by KOH treatment. In addition, the conductivity increased with increasing temperature, which could be explained by band overlap.

1. Introduction

Graphene holds promise as a next generation solid state device material because it has high carrier mobility, thermal conductivity, hardness and chemical stability [1–5]. In order to utilize graphene for practical electronic applications, it is necessary to control the carrier type. Techniques for doping graphene during the deposition process [6] and by adsorption [7, 8] have been reported; however, problems remain with both reproducibility and degradation. Recently, stable n-type conduction in bilayer graphene was reported, where potassium (K) doping was achieved by dipping the material in potassium hydroxide (KOH) solutions [9–11]. In these studies, Raman spectroscopy results implied that K atoms existed between graphene layers [9]. However, neither the distribution of K atoms nor the chemical and crystal structure of K-doped bilayer graphene has been revealed.

In the present study, to clarify the K atom distribution and structure in K-doped graphene, K doping of multilayer graphene rather than bilayer graphene was carried out. The distribution of K atoms in the stacking and in-plane directions of the KOH-treated multilayer graphene was characterized by means of time-of-flight
secondary ion mass spectroscopy (TOF-SIMS). In previous studies, the structure of K-intercalated nanographite and K-intercalated few-layer graphene was determined by x-ray diffraction (XRD) [12] and Raman spectroscopy [13, 14], respectively. X-ray photoelectron spectroscopy (XPS) is also an appropriate tool to evaluate the chemical structure of graphite intercalation compounds (GICs) [15]. Therefore, XRD, Raman spectroscopy and XPS were applied to elucidate the structure of KOH-treated multilayer graphene in the present study. In addition, the electronic properties were characterized by temperature-dependent conductivity measurements, and semiconductor-like conduction was observed, indicating an increase in conductivity by KOH treatment. Based on these results, conduction models for multilayer graphene with and without KOH treatment are discussed.

2. Experimental

K doping of multilayer graphene was carried out by a wet process using KOH (CAS: 1310-58-3) aqueous solutions [9–11]. Commercially available multilayer graphene on Ni foil (purchased from Graphenea Inc.) deposited by thermal chemical vapor deposition (CVD) was used. The typical thickness of the graphene measured by atomic force microscopy was approximately 40 nm. Using polymethyl methacrylate (PMMA) (CAS: 9011-14-7) as a support material, the Ni foil was etched in a 20 vol% iron chloride (FeCl₃) (CAS: 7705-08-0) aqueous solution at room temperature. After etching, the sample was rinsed in deionized (DI) water, and then floated on a KOH solution for 60 h. After rinsing with DI water, the sample was made to land on a quartz substrate in DI water. KOH-treated multilayer graphene was obtained after removal of the PMMA by acetone (CAS: 67-64-1). As a reference, multilayer graphene/quartz substrates were prepared without KOH treatment.

TOF-SIMS measurements were carried out to evaluate the distribution of K atoms in both the in-plane and stacking directions of graphene. For sputter etching, the accelerating voltage and current of the Cs⁺ ion beams were 1 keV and 250 nA, respectively. The cycle time for the sputtering was 70 μs. A Bi⁺ ion beam with an accelerating voltage of 25 keV and a current of 0.6 pA was used for the analysis. K⁺ gave higher counts than the limit of the system, and therefore 41K⁺ ions were evaluated in this study.

The crystal and chemical structures of the KOH-treated multilayer graphene were examined by XRD, Raman spectroscopy and XPS, and compared with the multilayer graphene without KOH treatment. The interlayer spaces of the samples were measured by XRD using Cu Kα (λ = 0.154 nm) radiation with 2 theta scanned from 2° to 60°. Raman measurements were performed using a confocal micro-Raman system. The laser wavelength and spot diameter were 488 nm and 1 μm, respectively. XPS was used to gain an understanding of the chemical structure. The base pressure of the system was less than 5 × 10⁻⁷ Pa. The x-ray source for XPS was monochromatic Al Kα (1487 eV). An aperture (110 μm in diameter) was used to limit the measurement area. The sample was grounded during the XPS measurements.

Titanium/gold (Ti/Au) electrodes were deposited on the four corners of the graphene surfaces by vacuum evaporation to measure the electrical properties. The thicknesses of the Ti and Au layers were 10 and 90 nm, respectively. The measurements were performed in vacuum (2 × 10⁻³ Pa) after thermal treatment at 473 K for 1 h to remove the adsorbed water. Temperature-dependent conductivity measurements were carried out in the temperature range of 300 to 473 K.

3. Results and discussion

Depth profiles of 41K⁺, C⁺ and SiO⁺ for the KOH-treated multilayer graphene are shown in figure 1(a). The sputtering depth was not estimated in this study; however, we determined the graphene/quartz interface as the point where the counts of SiO⁺ and C⁺ ions saturated (at approx. 290 sputtering cycles). 41K⁺ gave counts of about 10⁶ from the top surface to the graphene/quartz interface. From the TOF-SIMS depth profile, it was found that K atoms existed in the graphene films along the stacking direction. In our previous studies, it was not clear whether K atoms were adsorbed on the surfaces or existed at the graphene/substrate interfaces for a K-doped bilayer and stacked two-layer graphene [9, 10].

A TOF-SIMS intensity map of the 41K⁺ signal for the first 20 cycles is shown in the inset of figure 1(a). Although there were variations in the intensity of the 41K⁺ signals, the signals were obtained across the whole area. The TOF-SIMS results indicate that although K atoms are present throughout the full thickness of the KOH-treated multilayer graphene film, the in-plane doping level is not uniform, which is consistent with previous results for K-doped bilayer graphene [9]. A TOF-SIMS depth profile for the multilayer graphene after 5 h of KOH treatment is shown in figure 1(b) as a comparison. The 41K⁺ counts increased from 10⁷ near the top surface (at the beginning of the sputtering cycles) and then almost saturated at 10⁸ near the substrate. The K atoms diffused from the back side where the Ni foils were removed. Schematics of multilayer graphene with and without KOH treatment are shown in figures 1(c) and (d), respectively. This data indicate that KOH treatment
for 5 h was not sufficient to dope K atoms throughout the stacking direction. The K atoms are incorporated throughout the graphene after KOH treatment of 60 h. Hereafter, the results of XRD, Raman, XPS and resistivity measurements of the multilayer graphene are presented and discussed for the samples with 60 h of KOH-treatment.

The XRD patterns showed no major differences between multilayer graphene with or without the KOH treatment, as shown in Figure 2. Peaks due to (002) and (004) graphite planes are observed at 26.6° and 54.8°, respectively. The estimated interlayer spacings are 3.37 Å for both samples, which indicates that the interlayer spacing is not increased by the KOH treatment. No new peaks due to a GIC are observed after KOH treatment. In an earlier study on K-intercalated nano-graphite, shoulder peaks around 29° for a stage-2 K-GIC and 33° for a stage-1 K-GIC were reported, and the graphite (002) peak became broader [12]. However, in the present study, shoulder peaks are not observed for the KOH-treated multilayer graphene, as shown in the inset of Figure 2. The formation of GIC could not be determined using XRD.

Typical Raman spectra of multilayer graphene with and without KOH treatment are shown in Figure 3(a). Splitting of the G-band peak and disappearance of the 2D-band peak, as observed in K-GIC formation [13, 14], are not observed for the KOH-treated multilayer graphene. After the KOH treatment, the G-band peak shifts from 1568.0 to 1579.4 cm⁻¹ and broadening of G-band full width at half maximum (FWHM) from 23.7 to 24.8 cm⁻¹ occurs (Figure 3(b)). These results indicate that electron doping of the multilayer graphene took place by

![Figure 1](image1.png)

**Figure 1.** TOF-SIMS spectra of multilayer graphene samples following KOH treatment (a) for 60 h and (b) for 5 h. Schematic diagrams of K content in the graphene are depicted in (c) and (d).
KOH treatment [16]. The effect of K doping was less obvious in 2D band peak (figure 3(c)): the slight shift infers that change of electron density is in the order of $10^{13}$ cm$^{-2}$ or smaller [16]. The electric property of the KOH-treated graphene was characterized by conductivity measurement as described later.

Incorporation of K atoms in the multilayer graphene was further characterized by core level shift of carbon (C1s) and potassium (K2p) in XPS. The incorporated K atoms are expected to form either K-terminated edges and/or boundaries of graphene flakes, or K-GIC within the graphene layers [17]. Figure 4(a) compares XPS spectra of pristine and KOH-treated graphene with peak deconvolution results. The spectrum for the pristine graphene consists of peaks attributed to sp$^2$ carbon (284.8 eV), sp$^3$ carbon (285.5 eV), carbon oxides (C–OH for 286.4 eV and C–O–C for 287.6 eV), as well as π–π$^*$ transition (broad peak at 291.0 eV) [18]. No peak due to K is detected in the pristine graphene. In contrast, XPS spectrum for the KOH-treated graphene in figure 4 was separated into four additional component peaks: a peak at 283.5 eV attributed to K-terminated graphene, a new peak at 285.8 eV, and peaks at 292.2 eV and 295.0 eV representing K 2p$_{3/2}$ and 2p$_{1/2}$, respectively. The peak at 283.5 eV is interpreted as being associated with K-terminated graphene edges and/or boundaries: the K-termination results in a shift of the C1s peak to lower binding energy, due to dipole formation brought on by the different electronegativities of K (0.8) and C (2.5). The peak at 285.8 eV is considered to be a C1s peak.

Figure 2. XRD spectra of pristine and KOH-treated multilayer graphene samples. The inset shows an enlarged view of the spectrum for the KOH-treated sample, at angles between 24° and 40°.

Figure 3. Raman spectra of pristine and KOH-treated multilayer graphene samples. The spectra are plotted for 1000–3000 cm$^{-1}$ in (a) and enlarged to compare (b) the G-band peaks and (c) the 2D band peaks, respectively.
modified by neighboring K atoms: similar peak shift was reported for K-intercalated graphite [15, 19]. The XPS results suggested that K-terminated graphene exists in the KOH-treated multilayer graphene. The K concentration calculated from the XPS spectrum is approximately 1.5%. Figure 4 also indicates that KOH treatment results in decreasing of sp³ component, which implies that K atoms are selectively bound in a specific bonding site. Further analysis is being planned using synchrotron radiation XPS.

The XPS suggests that the K atoms are terminating the edges and boundaries of the graphene flakes. In addition, XRD and Raman suggest that long-range order of the graphene structure is maintained. Based on these results, the structure of the KOH-treated graphene is expected to be a mixture of K-terminated graphene flakes/domains (figure 4(b)) and original graphene structure (figure 4(c)). Although the XPS results were obtained from the near-surface region, it is considered that the proposed models can be applied to the whole multilayer graphene.

The temperature dependence of the conductivity of KOH-treated and pristine multilayer graphene is plotted in figure 5. KOH-treated graphene shows higher conductivity than pristine graphene at all temperatures. The conductivity of the KOH-treated sample at 300 K was calculated to be $1.8 \times 10^3$ S·cm⁻¹, which is approximately 50% higher than the value of $1.2 \times 10^3$ S·cm⁻¹ for the reference. This difference in conductivity is almost the same as that previously reported for bilayer graphene [9]. It should be noted that both the KOH-treated sample and the pristine graphene become more conductive as the temperature was increased, suggesting semiconductor-like conduction. This behavior has been explained in the literature using a two-carrier model with an overlap between the conduction and valence bands of few-layer graphene [20]. The temperature dependence of the conductivity can be described by the following equation:

$$\sigma(T) = C_1 k_B T \ln \left[ 1 + \exp \left( \frac{\delta E_0}{2k_B T} \right) \right]$$  \hspace{1cm} (1)$$

where $\delta E_0$ is the band overlap, $k_B$ is the Boltzmann constant and $C_1$ is a proportionality factor. Numerical fitting using equation (1) gives $\delta E_0$ values of 46.8 meV for pristine and 75.7 meV for KOH-treated multilayer graphene, respectively. The increase in $\delta E_0$ suggests that the overlap between the conduction and valence bands was increased by KOH treatment. This agrees with previous study on KOH-processed bilayer graphene, in which electron density in the graphene was increased by KOH-treatment [9]. The band overlap model is depicted in the inset of figure 5. Assuming that the Fermi level is fixed in the overlapping region, the conduction band below the Fermi level is occupied by free electrons. When the band overlap becomes larger, the density of occupied states increases, which results in a higher electron density. The increased electron density is also implied from the appearance of a shoulder at the lower binding energy side of the C1s peak in the XPS spectrum, as well as the up-
shift of the G band peak in the Raman spectrum. A detailed characterization of the band overlap requires an angle-resolved UPS analysis, which is currently unavailable.

The characterization results show that although the K distribution is inhomogeneous, K atoms exist throughout the multilayer graphene. Formation of K-GIC was not confirmed by the XRD and Raman results. The XPS results indicate that the KOH-treated graphene consists of original graphene structure and K-terminated graphene. The KOH-treatment resulted in increasing of electron density and decreasing of resistivity. These explanations are in agreement with previous reports on K-doped bilayer graphene [9] and K-doped stacked two-layer graphene [8]. For industrial applications, it is necessary to develop a control method to obtain appropriate structures. Detailed characterization of the materials using synchrotron radiation XPS and electrical measurements at low temperature are in progress.

4. Summary

In order to determine the K distribution and structure of K-doped graphene, K-doped multilayer graphene was prepared by a wet chemical KOH process. From depth profiles of $^{41}$K$^+$ ions in multilayer graphene obtained by TOF-SIMS, it was found that the K atoms were present in the KOH-treated graphene films along the stacking direction. By comparing two samples treated for 60 and 5 h, it was found that the K atoms defused from the back surface where the metal catalyst substrates were removed. XRD results suggested that interlayer spacing did not change by KOH treatment. Raman results inferred that the graphene was lightly doped by the treatment, which is evident from the up-shift of the G-band peak. In the XPS spectra, shoulder peaks due to K-C bonds appeared after the KOH treatment, which indicated that the K atoms were incorporated to graphene, and some K atoms formed K-terminated graphene layers. A decrease in resistivity was obtained by the KOH treatment. The temperature dependence of the resistivity implied semiconductor-like conduction, and a two-carrier model was presented as a possible mechanism for the increased electron density.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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