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Synthesis of Nitrogen-Doped Graphene via Thermal Annealing Graphene with Urea

Xin-jing Li[a], Xin-xin Yu[b], Jin-yang Liu[a], Xiao-dong Fan[a], Kun Zhang[b], Hong-bing Cai[b], Nan Pan[b], Xiao-ping Wang[a,b*]

a. Department of Physics, University of Science and Technology of China, Hefei 230026, China
b. Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

Chemical doping is an effective method to intrinsically modify the chemical and electronic property of graphene. We propose a novel approach to synthesize the nitrogen-doped graphene via thermal annealing graphene with urea, in which the nitrogen source can be controllably released from the urea by varying the annealed temperature and time. The doped N content and the configuration N as well as the thermal stabilities are also evaluated with X-ray photoelectron spectroscopy and Raman spectra. Electrical measurements indicate that the conductivity of doped graphene can be well regulated with the N content. The method is expected to produce large scale and controllable N-doped graphene sheets for a variety of potential applications.

Key words: Graphene, Doping, Conductivity, X-ray photoelectron spectroscopy, Raman spectrum

I. INTRODUCTION

Graphene, emerging as a true two dimensional material, has recently become one of the most promising materials for the electronic devices. This is because of its unique properties, such as high surface area, excellent conductivity, electron mobility, and the super chemical stability [1−8]. Unfortunately, the pristine graphene does not seem to be ready for the direct applications due to its gapless electronic structure. As a consequence, optimizing and modifying its electronic structure to obtain special characteristics is a very important task for its future implementation. In this regards, many strategies including chemical functionalization [9], electrochemical modification [10], and numerous hybrids nanocomposites [11, 12] have been reported. However, most of these approaches have been focused on producing graphene hybrids or multiple functionalities, and little attention has been paid to intrinsic modification of the graphene performance. On the other hand, doping with foreign atoms in the graphene, similar to that elaborated for the silicon-based technology, is a conventional and effective method to modify the graphene intrinsically, to tailor its electronic properties, to manipulate surface chemistry and to produce local changes to the elemental composition of host materials [13]. Recently, several approaches have been successfully demonstrated

to dope nitrogen atoms into graphene sheets to regulate its electronic properties and enhance its performance. For instance, Wei *et al.* prepared the N-doped gaphene by chemical vapor deposition [14]. Lin *et al.* developed a N-doping method through the ammonia plasma [15], and Long *et al.* report a N-doped graphene sheets obtained with combined chemical and hydrothermal reduction of graphene oxide [16]. Obviously, the chemical doping of graphene is an active area of research and new doping approach remains to be investigated.

Herein we describe a novel method to synthesize the nitrogen-doped graphene via thermal annealing graphene with urea. The graphene sheet with high level of nitrogen doping was achieved through the reaction between the surface of graphene and the N-containing groups released from urea at high-temperature. The different surface configuration of nitrogen and the thermal stability were also evaluated with X-ray photoelectron spectroscopy (XPS). The successful N-doping into graphene was also identified with the Raman spectrum and the electrical measurement.

II. EXPERIMENTS

The graphene was prepared by the chemical vapor deposition (CVD) method as previous report [17]. In brief, the copper foil purchased from Alfa was used as the substrate. After rinsed with acetone and deionized water and dried with flowing gas, the copper foil was put into a quartz tube with 25 mm diameter. The foil was first annealed at 1000 °C for 20 min (under hydrogen

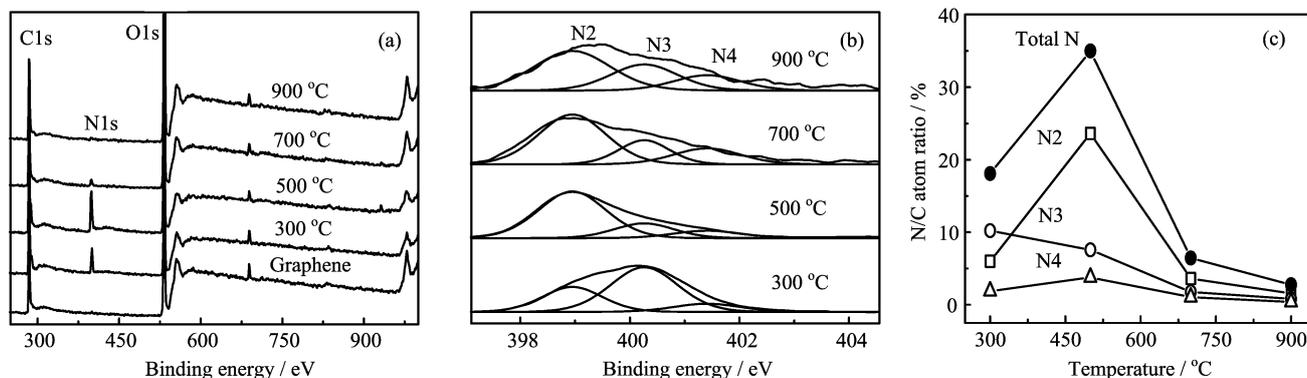*Author to whom correspondence should be addressed. E-mail: xpwang@ustc.edu.cn

FIG. 1 (a) XPS survey scan of graphene and N-doped graphene annealed at different temperature. (b) N1s spectrum of graphene doped at different annealing temperature, each can be deconvoluted by three Gaussian fitting. (c) Variation of total N, N2, N3, and N4 content in doped graphene with the annealing temperature.

gas flow of 100 sccm) to remove its surface oxide, and then the methane gas flow at 50 sccm was introduced into the tube, while the hydrogen gas flow was decreased to 30 sccm with the tube vacuum kept at 2.4−2.8 kPa. After growth for 30 min, the temperature was cooled rapidly while the hydrogen gas flow was kept at 50 sccm.

For transferring the as-prepared graphene on the Cu foil to the SiO_2/Si substrate, a thin PMMA film was first spun onto the graphene surface, and then the Cu foil was dissolved away with nitric iron acid solution. After cleaned with plenty of deionized water, the graphene covered with PMMA film was transferred onto the SiO_2/Si substrate and dried on the plate stove at 180 °C. The PMMA was washed off afterwards with acetone.

N-doped graphene was achieved by annealing the graphene at high temperature with urea. The urea was purchased from Sigma-Aldrich and used as the nitrogen source. It is known that the ammonia and cyanic acid can be released from urea at high temperature [18], which will be absorbed onto and react with the graphene. In the annealing process, the graphene was first placed in the end of a small quartz tube with the diameter of 15 mm and the length of 25 cm, in which a quantity of 0.5 g urea powder was loaded. After that, the tube was closed by another large quartz tube with the diameter of 20 mm, and both tubes were inserted into the alumina furnace. The furnace was heated up to the set-point temperature and maintained for 5 min, and then cooled gradually to the room temperature.

The doped graphene was characterized by the XPS, Raman spectroscopy and electrical measurement. Note that, the urea remnant on the graphene surface can be well removed through washing the graphene with an amount of deionized water. The XPS measurement was performed using an ESCALAB 250 X-ray photoelectron spectrometer with a monochromatic Al Kα radiation. Raman spectra were obtained by a LABRAM-HR Raman spectrometer with an excitation wavelength of 514.5 nm and power of ∼1 mW. The focused laser

spot is about 10 μm. For all the Raman spectra, the baselines have already been subtracted. The electrical properties were measured by Keithley 4200 and the Lakeshore probe station was under the vacuum of 0.1 mPa. *I-V* curves from a series of the samples was measured between 5 and −5 V, and the average and standard deviation of the conductivity for the doped graphene have been calculated.

III. RESULTS AND DISCUSSION

N-doped graphene was first confirmed by the XPS characterization. As seen in Fig.1(a), the survey scan spectrum of XPS shows the presence of the C1s, O1s, and N1s core levels in the doped graphene, while no evidence of other impurities can be found. Furthermore, the N doping contents show temperature dependent, it increases with the increase of the temperature and reaches the highest value at 500 °C, but then decreases with further increase of the temperature. In order to rule out the possibility that the N content originated from the urea reacted with the SiO_2, the SiO_2 substrate was treated using the same annealing procedure at 500 °C for 5 min and N1s signal can not be observed in XPS. Therefore, we can conclude that the nitrogen was indeed doped onto the graphene structure. Note that, with our proposed doping approach, the maximum atom ratio of N to C (N/C) can reach 35%, much higher than 17% by annealing GO with ammonia [19], indicating the urea is an efficient dopant to form the N-doped graphene.

When nitrogen doped into graphene, several configurations will form to result in different surface chemical structures, which can be characterized by the core level of nitrogen [20]. Figure 1(b) shows the N1s peaks of the graphene doped at different temperature. As seen, the N1s signal shows broad feature and can be further deconvoluted into three components, each is well fitted with a Gaussian function. The first component with
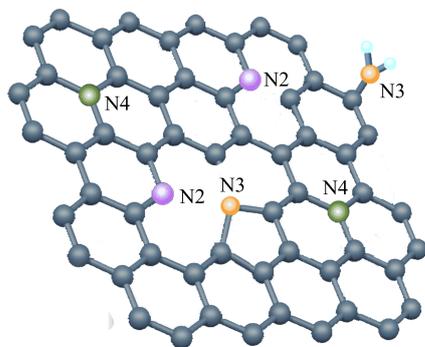
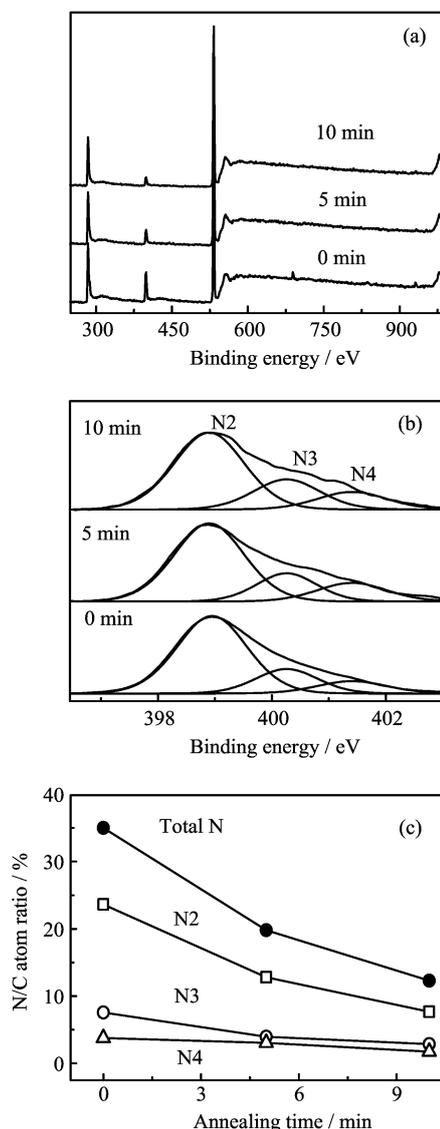FIG. 2 Schematic diagram of nitrogen species in the doped graphene.

FIG. 3 (a) XPS spectra of doped graphene treated in Ar with different time at 500 °C. (b) N1s spectrum of graphene doped at different temperature, each can be deconvoluted by three Gaussian fitting. (c) Variation of the contents of nitrogen and N2, N3, N4 with the treated time.

the peak at 401.4 eV can be ascribed to the graphitic-N (assigned to N4, in Fig.2), corresponding to N incorporated into the graphene plane by replacing a carbon atom [20]. The second component with the peak position at 400.3 eV (assigned to N3, in Fig.2) may be contributed to amide, amine, or pyrrolic N [21]. This configuration frequently occurrs and is located in the defect or the boundary of the graphene. The third component with the peak position at 398.9 eV (assigned to N2, in Fig.2) can be indexed to pyridinic-N [13].

Figure 1(c) clearly shows the variation of total N content and the different component of N in the doped graphene with the annealing temperature. The different temperature dependence for the various nitrogen configurations of N2, N3, and N4 may arise from their different thermal stability. As to clarify this point, we treated the doped graphene (obtained with annealed in urea at 500 °C for 5 min) again in the Ar ambience at 500 °C with different time (5 and 10 min) and the XPS results are shown in Fig.3(a). As seen, the content of N in the sample will drop rapidly with increasing the annealing time, confirming that the nitrogen on the graphene is not very stable at high temperature. The decreasing of N content is probably due to either desorption of the amide and the amine from doped graphene or break of carbon nitrogen bonds of N3 and N2 configurations. Figure 3 (b) and (c) further show the evolution of N2−N4 configurations with the treated time, from which we can conclude that the N4 is the most stable while the N2 is the most unstable.

Based on the results of Fig.1(c) and Fig.3, the temperature dependence of different configuration of nitrogen on the doped graphene can be understood as follows. It has been reported that the species, such as −NO, urea species, biuret, CYA, and ammelide, can be released from urea and formed readily on the graphene at low temperature (<300 °C) [18], this can bring about the content of N3 to be dominant at the low temperature. However, these species became unstable and desorbed from the graphene when the temperature is higher than 300 °C [18], resulting in the decrease of the N3 with the temperature. On the contrary,

when annealed at 500 °C, both the N2 and N4 might overcome the high barrier to react with the graphene and cause the increasing of their proportion. When annealed at higher temperature, however, the carbon-nitrogen structure can be destroyed, resulting in the rapid deceasing of the content of N2 and a little loss of N4.

Figure 4(a) shows the Raman spectra of the samples doped at different temperature. As seen, both G and 2D Raman peaks occur on all samples. The G-band at ~1580 cm^{-1} is due to the doubly degenerate E_{2g} mode at the Brillouin zone center of graphene [22], and the 2D peak at ~2700 cm^{-1} originates from the double resonance process activated second-order Raman scattering
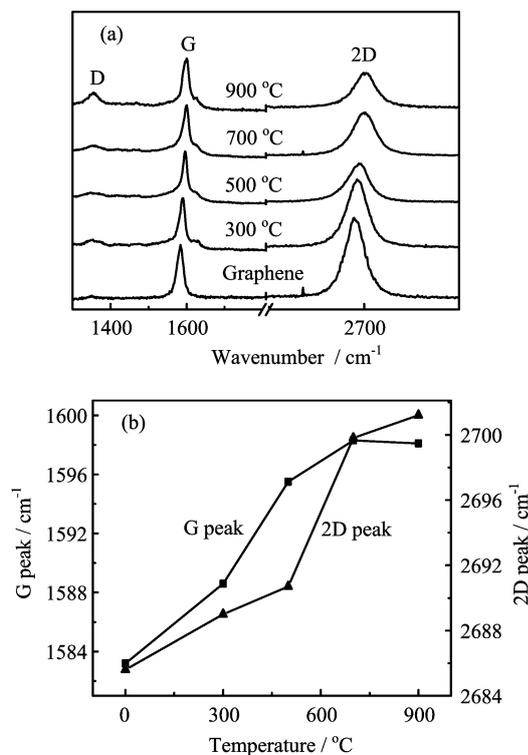
FIG. 4 (a) The Raman spectra and (b) the blueshift of G and 2D peaks for pristine graphene and the doped graphene obtained at different temperature.

near the boundary of the Brillouin zone of graphene [23]. For pristine graphene, the intensity ratio of I_{2D} to I_G is estimated to about 2.5, confirming it a single layer graphene [24]. For the doped graphene, the D-band at ~ 1350 cm^{-1}, an indicator of the disorder or defect in the smaple [25, 26], is very weak for the annealing temperature from 300 °C to 700 °C. This result reveals that our method is more moderate than that using plasma [15]. However, the D band can be found obviously for the sample annealed at 900 °C.

Figure 4(b) shows that both of peak positions of G and 2D band will present upshift with increasing the annealing temperature. The behavior, at first sight, can be naturally ascribed to the charge transfer from the nitrogen or N-contained groups to the graphene. However, this explanation is not consistent with the result shown in Fig.1(c), in which the nitrogen content decreases as the annealing temperature is higher than 500 °C. Therefore, the cause of the discrepancy between the observed upshift of Raman peak and the decreasing charge transfer above 500 °C should be explored. As observed in Fig.4(a), the amount of the defect and disorder, which is the origin of D band, is expected to become more when the annealing temperature is increased. Considering that the defect such as topological impurity of pentagon rings will induce the constriction of carbon-carbon band and increase the vibration frequency of the bonds [27], it is reasonable to contribute
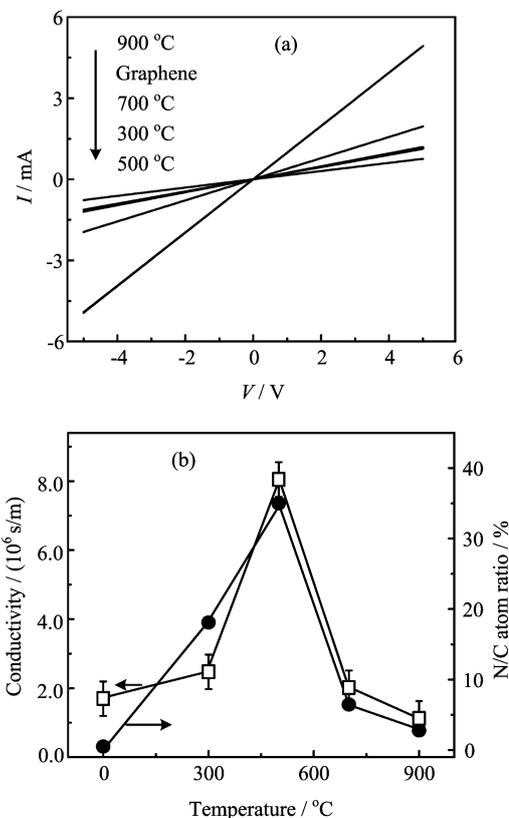

FIG. 5 (a) *I-V* curves of pristine and doped graphenes annealed at different temperature. (b) The conductivity and the N contents of doped graphene vary with the annealing temperature.

the upshift of G and 2D peak to the local strain induced from the defects in the doped graphene. Consequently, we believe that the charge transfer is the dominant reason for the upshift of Raman peaks at low annealing temperature due to the high doping N content. However, for the high annealing temperature, because less N content can remain on the graphene and more defects appear in the graphene, the intrinsic strain in the doped graphene becomes the dominant reason for the upshift of Raman peaks.

We also investigate the electrical properties of the doped graphenes by *I-V* measurement. This was carried out using the gold electrodes with separated space ~ 8 mm. As seen in Fig.5(a), all *I-V* curves show good linear feature, indicating the metallic behavior of the doped graphene and the negligible Shottkey barrier existing between the graphene and the electrode. Furthermore, based on the *I-V* curve, the calculated conductivity and its uncertainty of doped graphene are given in Fig.5(b). As seen, the conductivity of pristine graphene is about 10^6 s/m, which is consistent with the previous report [28]. However, the conductivity of doped graphene increases first with the annealing temperature and arrives at maximum value of $\sim 8 \times 10^6$ s/m at 500 °C, and then decreases with increasing tempera-

ture. Moreover, we find that the variation of the conductivity with the annealing temperature is very similar to the total N content as shown in Fig.1(c), which is also re-plotted in Fig.5(b). Assuming that the carrier concentration of doped graphene is dominated by the charge transferring from the nitrogen or N-contained groups, based on $\sigma = ne\mu$, we can speculate that the charge transfer ability is independent of the N configuration and the mobility of the doped graphene does not degrade even after treated at high temperature. It suggests that annealing graphene in the urea is a simple, low-cost, and effective method to realize the doped graphene, which can further find wide applications for the graphene-based materials and devices.

IV. CONCLUSION

We synthesize the nitrogen doped graphene by a simple and low-cost method with the nitrogen source released from the urea under high temperature. XPS results show that three N configurations, N2, N3, and N4, can occur on the doped graphene. Due to their different activity and thermal stability, the content can be well controlled with the temperature: N3 is abundant at 300 °C while N2 becomes dominant for the high temperature. Moreover, the electrical measurements indicate that the conductivity of doped graphene can be well regulated by the N doped content, identifying that the charge transfer occurred between the N-contained group and the graphene. This simple, low-cost and effective method can help to realize the doped graphene for many applications.

V. ACKNOWLEDGMENTS

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