Doping Graphene by Chemical Treatments Using Acid and Basic Substances

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Abstract

We prepared single-layer graphene films through mechanical exfoliation of Kish graphite and chemical vapor deposition techniques. These samples were treated in nitric acid, sulfuric acid, sodium hydroxide and ammonium hydroxide solutions to induce doping. We used Micro Raman Spectroscopy before and after the chemical functionalization to monitor differences in the Raman spectrum. We found shifting for both G and 2D peaks of graphene and a significant upshifting in samples treated with sulfuric acid, similar to those reported for nitric acid.

1. Introduction

Graphene as a zero band gap semiconductor is not able to be incorporated into electronic devices as other semiconductors do, such as silicon or gallium arsenide [1]. A lot of effort has been invested to open a band gap in graphene or to shift its Fermi level. Doping is an alternative way to tailor electronic properties of graphene. Doping in graphene can be induced by substrate [2], by substitution with other atoms such as nitrogen or boron [3], applying an electric field [4], or by absorbing molecules or atoms on graphene surface [5]. For the last case, nitric acid (HNO_3) has served to obtain p-type graphene [6] and ammonia was used to produce n-type graphene through electrothermal reactions [7]. Also, when a thin film of fullerene C_{60} is deposited on few layer graphene the resulting system shows negative photoconductivity and both p- and n-type doping depending on the intensity of illumination [8].

Because graphene can easily adsorb molecules on its surface, we use several solutions to search a comparable

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or better doping substance than HNO_3. Nitric and sulfuric acids are commonly used for the activation of a variety of carbonaceous materials and, on the other side, the appearance of a ferromagnetic behavior of graphite by sulfuric acid (H_2SO_4) treatments has been reported [9]. One of the main findings of the present work is that by the use of a simple method, H_2SO_4 produces an efficient doping in graphene. To our knowledge, this is the first time that such effect is reported.

For the study of doping in graphene, Raman spectroscopy has resulted to be a suitable nondestructive and powerful quantitative technique [4] [10] [11]. For n-type graphene, using adsorption of molecules with electron donating groups, G band downshifts [12] [13]. In p type doped graphene using adsorption of molecules with electron withdrawing groups, G band upshifts [12] [14]. In both cases, 2D band upshifts [14].

2. Experimental Details

For comparison purposes, two kinds of graphene samples were used in the present work: samples of graphene obtained by mechanical exfoliation of Kish graphite using adhesive tape and by chemical vapor deposition method (CVD). For CVD graphene samples, copper foil pieces of 1 cm × 2 cm were used as substrates, and a mixture of hydrogen and methane as the carbon source was used at ambient pressure and 1000˚C. After CVD synthesis, one side of the sample was spin-coated with PMMA (46 mg/ml) and annealed in a furnace at 160˚C for 5 minutes to relax the PMMA film. Copper was removed with a ferric nitrate solution and then PMMA/graphene film was put on top of a silicon substrate with 306 nm of silicon oxide. Finally, PMMA was etched with acetone.

The samples were immersed during a period of time of 24 hours in different aqueous solutions: nitric acid (HNO_3 at 65.9%) [6], sulfuric acid (H_2SO_4 at 65.9%), sodium hydroxide (NaOH at 2 M) and ammonium hydroxide (NH_4OH at 29%). After this treatment, the samples were rinsed for some seconds in deionized water to eliminate the excess of the chemicals.

The graphene layers were pre-identified using optical contrast and then corroborated using Raman spectroscopy. For Raman characterization a Nicolet Almega XR Spectrometer and 532 nm laser excitation was used, to avoid thermal effects we just used 2 mW of laser power. Raman spectra were taken in the pristine state and after chemical functionalization on the same sample, being the reported numerical results an average taken on different samples.

3. Results and Discussion

3.1. Exfoliated Graphene Samples

In **Figure 1(a)** Raman spectra of several exfoliated graphene samples are shown. It can be observed in **Figure 1(b)** that Pos(G) and Pos(2D) shift when graphene is functionalized. Because both G and 2D peaks upshift when HNO_3, H_2SO_4 and NaOH are used, we can say that these solutions produce p-type graphene [12]-[14]. The most important shifting is achieved with HNO_3 and H_2SO_4, corroborating the good performance of nitric acid as a doping agent as has been reported in the literature [6]. Doping using NaOH and NH_4OH has not been reported yet. We also show in **Figure 1(c)** the average of Pos(G) for each case and their corresponding Fermi energy (E_F) and carrier concentration (n) calculated using the following equations [15] [16]:

$$\left| E_F\left(\text{eV}\right) \right| = \left[\text{Pos}\left(G\right)\left(\text{cm}^{-1}\right) - 1580 \right] \Big/ 42 \tag{1}$$

$$n\left(\text{cm}^{-2}\right) = \left(E_F / \hbar v_F \right)^2 \Big/ \pi, \tag{2}$$

where v_F is the Fermi velocity and $\hbar$ is the Plank constant divided by 2π, here we use $\hbar v_F \approx 7.24 \times 10^{-8}$ eV·cm. Equation (1) is valid for the laser wavelength used in this work [17]. Using HNO_3 and H_2SO_4 a maximum carrier concentration of around 7×10^{12} cm^{-2} in exfoliated graphene samples is obtained, in comparison, doping produced by NH_4OH is almost negligible. It is proposed that in the case of H_2SO_4, H^+ is responsible for p-type doping in graphene [9].

Finally, as an important issue we investigate the doping effect of ferric nitrate in exfoliated samples because this substance is commonly used to dissolve copper in CVD samples. Interestingly, we did not find any significant doping effect in these samples and the question remains why CVD graphene is typically p doped [18].

3.2. CVD Graphene Samples

In **Figure 2(a)** Raman spectra of different functionalized samples are shown and in **Figure 2(b)** the corresponding
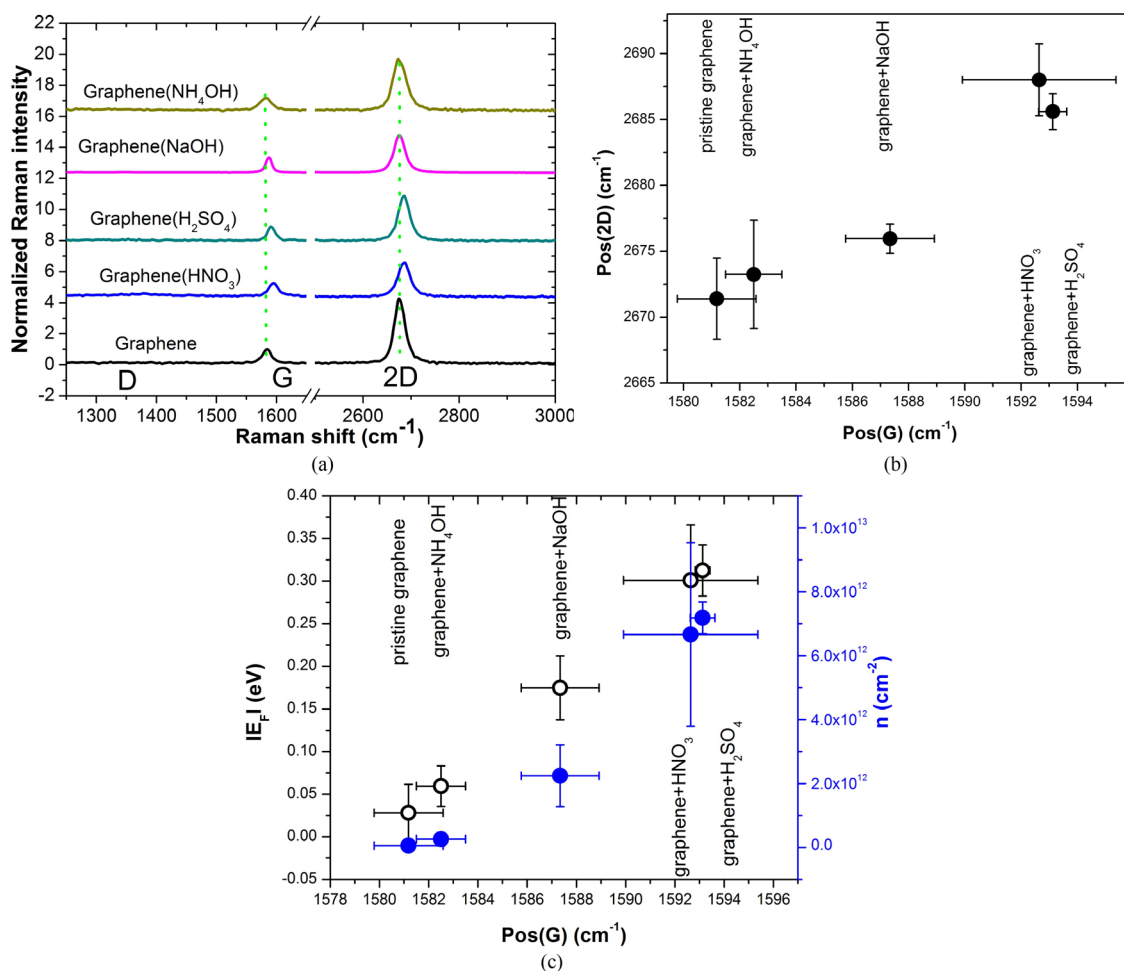
Figure 1. Exfoliated Graphene: (a) Raman spectra of graphene before and after one day of chemical functionalization; (b) Position of 2D peak versus position of G peak are plotted; (c) Fermi Energy and the carrier concentration as a function of Pos(G) are shown.

shifting of the G and 2D bands are presented. In the case of treatment with NH_4OH, it appears that n-type doping is obtained because a systematic downshift of the G band is observed, but care should be taken because measured values are within the resolution of the Raman equipment, which is 4 cm^{-1}. Doping with HNO_3 and H_2SO_4 in CVD samples produced p-type graphene but the shifting of the G and 2D bands are smaller than those obtained for exfoliated graphene samples. It should be noted that treatments using NaOH were not possible in CVD samples because the carbonaceous film immediately detached from the substrate while it is immersing in the NaOH solution, probably due to the poorer adhesion compared to the exfoliated samples and because this solution attacks the silicon oxide layer. In **Figure 2(c)** a plot of the calculated values of the Fermi energy and the carrier concentration are presented. We found that the values of these parameters are smaller than those calculated for exfoliated samples (see **Figure 1(c)**).

In general, the amount of doping is better in the case of exfoliated graphene compared to CVD samples. A possible explanation of this difference is the use of PMMA during the transfer process of CVD samples, because it is well known the existence of residuals of this substance on the samples, even when careful cleaning processes are used [19] [20]. We believe that the existence of PMMA residuals on the CVD samples avoid an effective charge transfer between dopants and graphene.

4. Conclusion

In this work, we have shown that aqueous solutions of sulfuric and nitric acids have better effects of functionali-
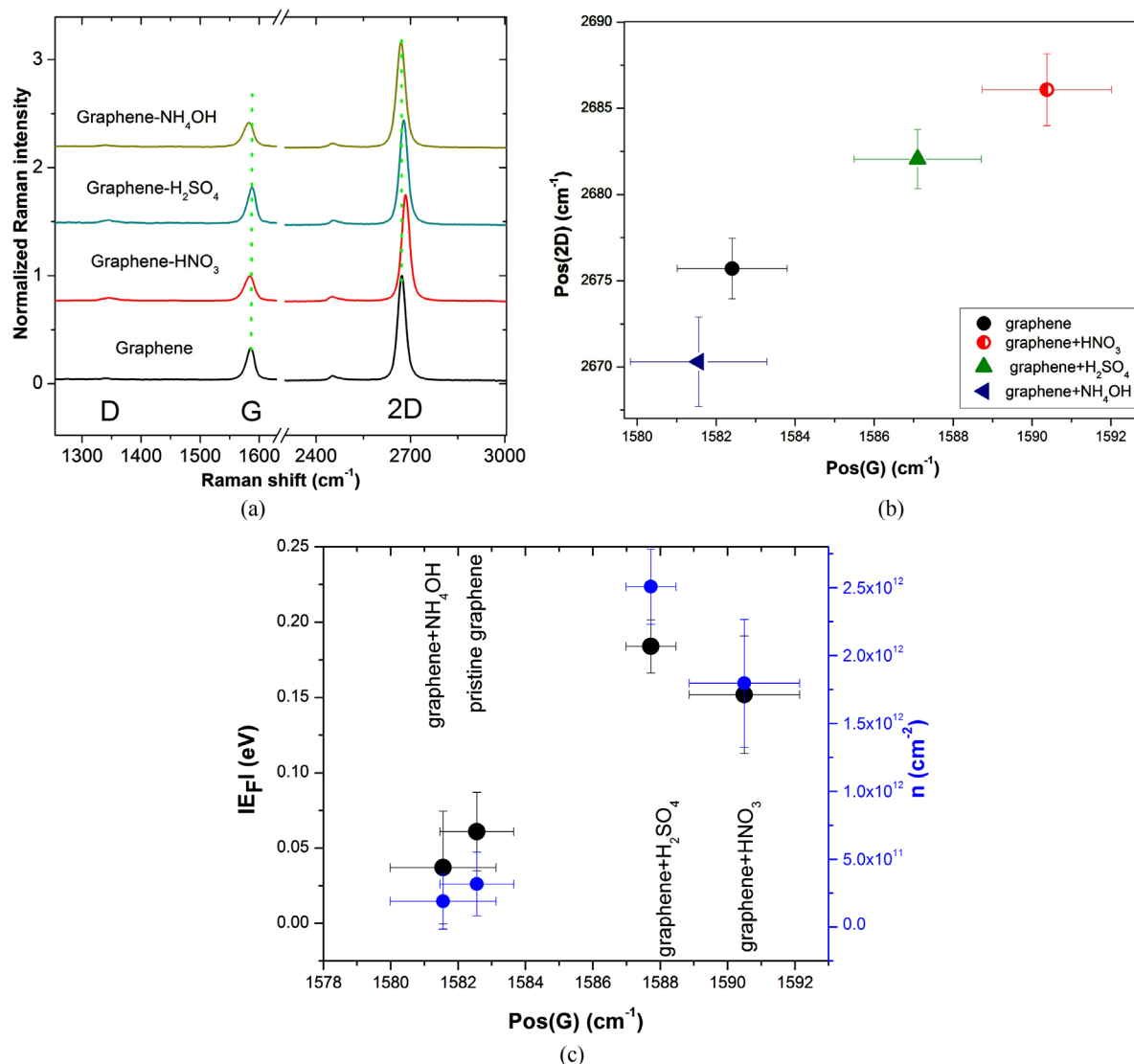
(a)

(b)

(c)

Figure 2. CVD Graphene: (a) Raman spectra of functionalized graphene; (b) Pos(2D) versus Pos(G) of functionalized graphene, and (c) Fermi Energy and carrier concentration as a function of Pos(G).

zation in graphene compared to ammonium and sodium hydroxides. The doping effect of sulfuric acid is comparable to nitric acid and this is the first time that the doping effect of sulfuric acid is reported. Analysis of the shifting of the G and 2D bands of the Raman spectra let us to conclude that the effect of chemical treatments produce p-type doping and a major effect is produced in exfoliated samples compared to that obtained in CVD graphene samples.

Acknowledgements

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