

Microarticle

Effects of nitrogen-dopant bonding states on liquid-flow-induced electricity generation of graphene: A comparative study

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ABSTRACT

We fabricate, measure and compare the effects of the bonding states of dopant nitrogen atoms in graphene devices, specifically on the liquid-flow-induced electricity by these devices. We find that nitrogen doping enhances the voltage induced by liquid flow regardless of the nitrogen bonding state. However, different nitrogen bonding states affect graphene's conductivity differently: while graphitic nitrogen is suitable for electricity-generation applications, pyridinic nitrogen is hopeless for this purpose, due to the formation of symmetry-breaking defects of the latter.

Introduction

Energy harvesting has been widely recognized as an important topic in recent years. Among the novel energy-harvesting methods reported [1–3], liquid-flow-induced electricity generation stands out as a mechanically non-degradable strategy that targets a variety of natural bodies of water—e.g., currents in ocean, river, waterfalls, rain, etc.—as a viable energy source. In this article, we focus on graphene as the energy-harvesting medium. Specifically, we investigate the effects of nitrogen doping on the electricity-generating capabilities of graphene. We discuss the contributions of the bonding states of nitrogen atoms in graphene as a follow-up report on previous research [4,5].

Methods

Graphene was synthesized by established chemical-vapor-deposition method [6,7], and then transferred onto silicon substrates. The devices were completed by fabricating electrodes onto these graphene/Si substrates at a separation distance of 10 mm. The doping of nitrogen in graphene was carried out using a custom neutral-beam (NB) system

[8]. We studied two types of nitrogen-dopant atoms with specific bonding states in graphene: graphitic and pyridinic nitrogen. While graphitic nitrogen atoms are located in the plane of graphene substituting the carbon atoms, pyridinic nitrogen atoms are located either above point defects, or at the graphene edge as shown Fig. 1(a). Based on our previous investigation, bonding-state selective synthesis of nitrogen doped graphene is possible by energy-controlled nitrogen NB, which produces graphitic and pyridinic nitrogen dopants at NB energies of $E_{NB} = 7$ eV and $E_{NB} = 13$ eV, respectively [8,9]. The NB fluxes under both these energy conditions are comparable, and the treatment time for doping is 1 min. This method yields doping concentration of about 0.5% for both nitrogen dopant types. Comparison between graphitic and pyridinic nitrogen for electricity generation was done by releasing a deionized (DI) water droplet from a height of 10 cm (Fig. 1(b)). The generated voltage was then recorded by an oscilloscope (Tektronix, TDS2004C) every 0.04 s.

Results and conclusions

Both pyridinic and graphitic nitrogen dopants enhance liquid-flow-induced voltage in graphene. The spike-like signals in Fig. 2(a) indicate

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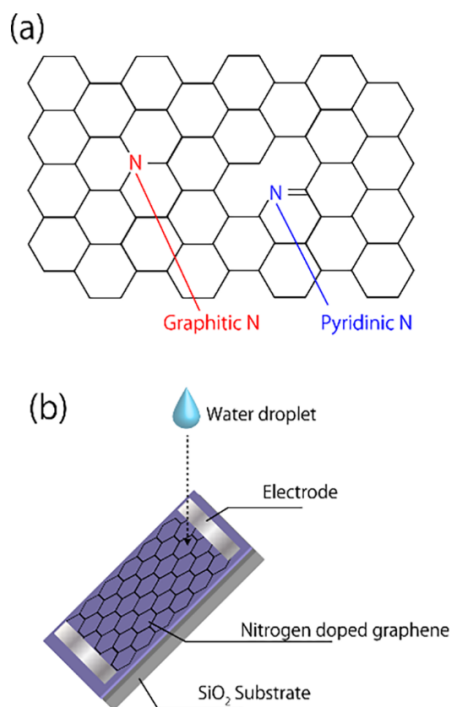


Fig. 1. (a) Chemical structure of graphitic and pyridinic nitrogen in graphene. (b) Schematic illustration of the experiment. Volume of DI water droplet, distance between electrodes, tilted substrate angle and the release height are 0.1 ml, 10 mm, 45 degrees, 10 cm, respectively.

the voltage induced at the interface between DI water and nitrogen-doped graphene. These spike-like signals appear just after each water droplet makes contact with graphene. On pristine graphene, a single water droplet induces a voltage $V = \sim 80$ mV. In contrast, the voltage induced at both types of nitrogen-doped graphene is approximately

three times greater in magnitude ($V = 230\text{--}240$ mV). The enhancement effect of nitrogen doping on voltage generation is explained by the surface charging of graphene at the nitrogen-dopant atoms. Initially, we expected the different bonding states of the graphitic and the pyridinic nitrogen atoms to affect the liquid-flow-induced voltage in graphene differently; however, our results in Fig. 2(a) show no such effect. Therefore, we propose that the observed voltage-induction enhancement is caused by the nitrogen atoms acting as electron donors, thus modifying the surface charge of graphene.

Both pyridinic and graphitic nitrogen doping cause resistance increase in graphene; however, pyridinic nitrogen causes a much larger resistance increase compared with graphitic nitrogen (Fig. 2(b)). We propose that the magnitude difference in resistance change is caused by the respective geometric constraints of the two nitrogen bonding states. Pyridinic nitrogen atoms are located at graphene's edge, forming point defects that disrupt graphene's π -system upon doping, causing the large resistance increase—i.e., conductivity decrease—in graphene (Fig. 2(c)). On the other hand, graphitic nitrogen atoms, located in graphene's plane, only cause a slight increase in graphene resistance via carrier scattering. The output power of the graphene samples were estimated and shown in Fig. 2(c). Graphitic nitrogen doped graphene shows 1.3 μ W, which it is ~ 1.5 times higher compared with pristine graphene (0.89 μ W). On the other hand, the output power from pyridinic nitrogen-doped graphene is negligible (0.01 μ W). Here, graphene's conductivity is significantly reduced by the geometric constraints of the pyridinic nitrogen.

In conclusion, comparison between graphitic and pyridinic nitrogen for flow-induced electricity generation was carried out as follow-up study of our previous results. Both graphitic and pyridinic nitrogen enhance comparable liquid-flow-induced voltage in graphene, and the generated voltage seems to be tolerant of the defects in graphene. However, pyridinic-nitrogen-doped graphene is not suitable for power generation devices: the geometric constraints of the pyridinic nitrogen degrade graphene's electric conductivity too much for this purpose. When the doped graphene is used as current path, the conductivity should be secured to obtain electrical current and power.

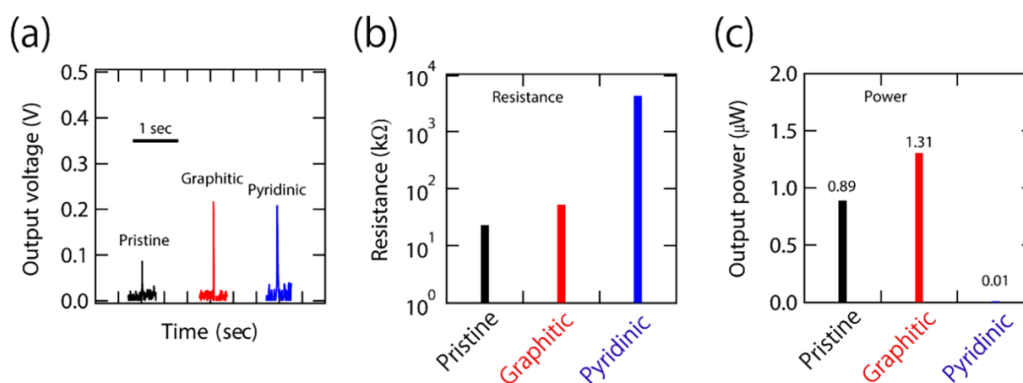


Fig. 2. (a) Typical signal of generated voltage. (b) Resistance between electrodes. (c) Estimated output power from each graphene sample.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rinp.2019.01.023>.

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