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Flow-induced voltage generation in non-ionic liquids over monolayer graphene

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To clarify the origin of the flow-induced voltage generation in graphene, we prepared a new experimental device whose electrodes were aligned perpendicular to the flow with a non-ionic liquid. We found that significant voltage in our device was generated with increasing flow velocity, thereby confirming that voltage was due to an intrinsic interaction between graphene and the flowing liquid. To understand the mechanism of the observed flow-induced voltage generation, we systematically varied several important experimental parameters: flow velocity, electrode alignment, liquid polarity, and liquid viscosity. Based on these measurements, we suggest that polarity of the fluid is a significant factor in determining the extent of the voltage generated, and the major mechanism can be attributed to instantaneous potential differences induced in the graphene due to an interaction with polar liquids and to the momentum transferred from the flowing liquid to the graphene. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792702>]

The advance of the nanotechnology highly has deduced novel mechanisms of energy generation using nanomaterials.^{1–3} As one of feasible mechanisms, experimental studies and theoretical interpretations have demonstrated that flow-induced voltage can be generated when graphitic surfaces (carbon nanotubes, graphene, etc.) are immersed in a flowing liquid.^{3–17} In 2003, Sood *et al.* reported that voltage can be generated from a film of single-walled carbon nanotubes (SWCNTs) in a flowing liquid.³ Similarly, it has been reported that multi-walled carbon nanotubes (MWCNTs) that are highly aligned to the flow direction can produce a higher voltage than non-aligned SWCNTs.⁸ We also reported that semiconducting SWCNTs (s-SWCNTs) can produce voltages that are three times higher than those in metallic SWCNTs (m-SWCNTs) in flowing liquid.¹² Recently, two studies on energy harvesting from liquid flow on graphene reported contradictory conclusions. Dhiman *et al.* showed that a graphene surface of $30 \times 16 \mu\text{m}^2$ surrounded by four patterned electrodes (Ti/Au, 3/30 nm) could generate a peak voltage of ~ 25 mV in 0.6 M HCl flowing solution.¹⁶ In sharp contrast, Yin *et al.* reported that electrode-solution interactions were a main voltage generation mechanism rather than interaction between graphene and the ionic water flow.¹⁷ All of the previous studies employed samples whose electrodes were aligned parallel to the liquid flow and only ionic solutions, including water, HCl, NaCl, etc. Here, we investigated the influence of graphene on voltage generation with new samples, which were aligned perpendicular to liquid flow, using non-ionic liquid. We systematically varied several important experimental conditions, including flow velocity, electrode alignment, liquid polarity, and liquid viscosity. As a result, we discovered new physical phenomena related to voltage generation on

graphene. Based on our findings, we suggest the polarity effect and an instantaneous potential difference on the graphene as plausible mechanisms for voltage generation.

In this work, we used monolayer graphene that was synthesized on $70 \mu\text{m}$ Cu foil inside a chemical vapor deposition (CVD) chamber, as reported previously.¹⁸ Figure 1(a) shows the Raman spectrum of a monolayer of graphene. The intensity ratio of the G and 2D peaks was 2.5–3, indicating monolayer graphene.¹⁹ The resistance of the graphene was ~ 1 k Ω . Electrodes were fabricated by the standard technique of photolithography on glass wafers. The metal patterns consisted of a 40-nm-thick layer of Au combined with a 10-nm-thick Cr layer for adhesion. The graphene was transferred onto electrodes ($5 \times 5 \text{mm}^2$). A polydimethylsiloxane (PDMS) block was sealed to the glass surface to complete the microfluidic chip, as shown in Figure 1(b). The schematics in Figure 1(c) show several samples in these experiments. Five kinds of samples were prepared, varying the presence of graphene in the chip and exposure of the electrode to flowing water (type-1: the electrodes are not exposed to flow in the absence of graphene; type-2: the electrodes are exposed to flow in the absence of graphene; type-3: both graphene and the electrodes are exposed to flow; type-4: the graphene sample whose electrodes (aligned perpendicular to the flow) are not exposed to flow; and type-5: the graphene sample whose electrodes (aligned parallel to flow) are not exposed to flow). A schematic of the experimental layout is depicted in Figure 1(d). A syringe was filled with solutions and attached to the inlet using a tube. The syringe, driven by a syringe pump (Legato 110, KD Scientific Co.), injected the fluid to immerse the graphene and then maintained fluid flow at a well-controlled rate. The fluid flow rate inside the microfluidic channel was controlled by adjusting the injection rate. The fluid at the exit of the PDMS was collected into a sump tank. The flow-induced voltage was measured in real time by

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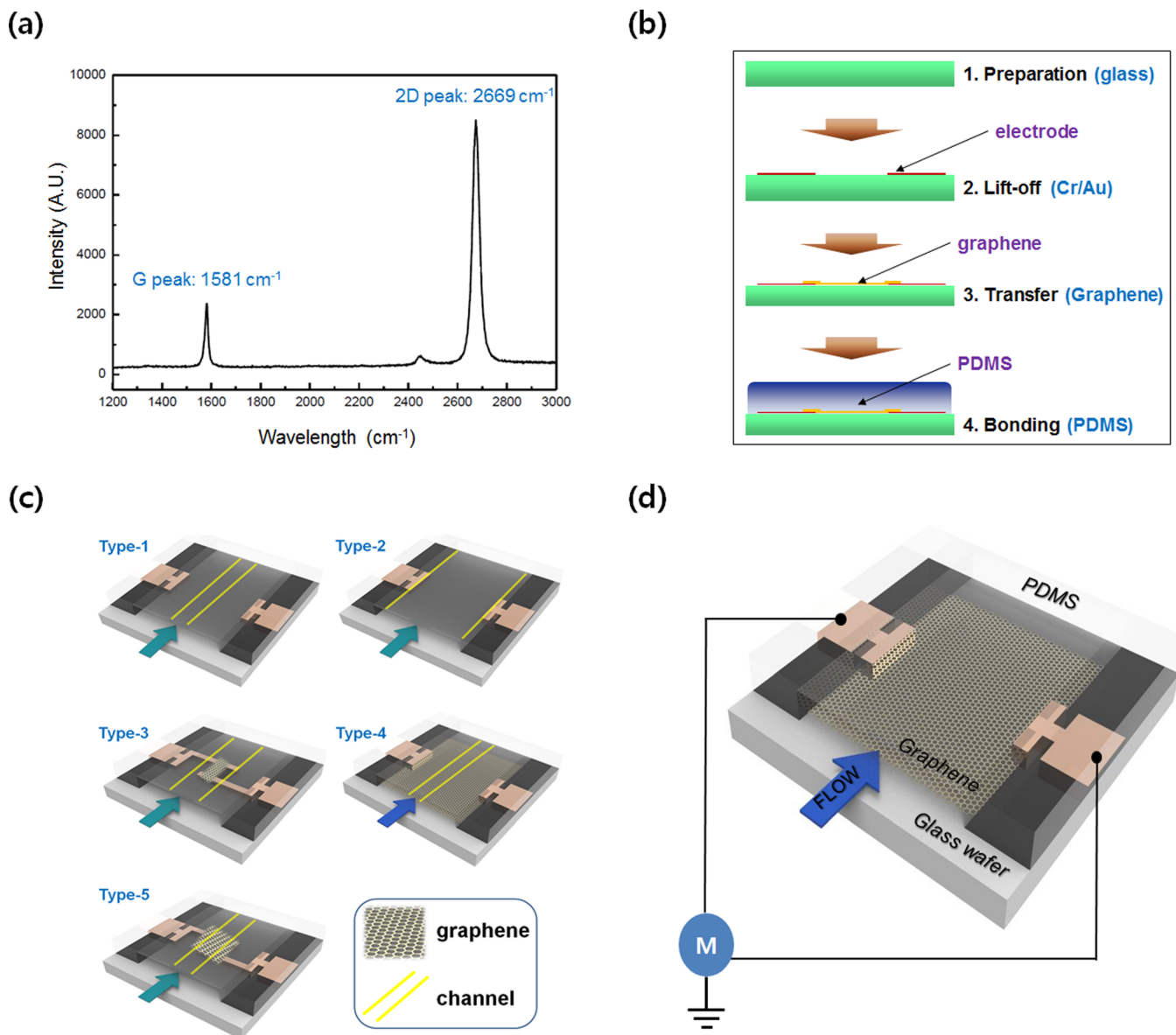


FIG. 1. (a) Raman spectra of monolayer graphene (514 nm wavelength excitation). (b) Fabrication process of the graphene sample. (c) Five kinds of samples according to the exposure of the electrode to the flow, existence of the graphene, and the alignment of the electrode to the flow. (d) Schematic illustration of the experimental setup.

a digital multimeter (DM 2002, Keithley Instruments) connected to a data acquisition system. All experiments were carried out at room temperature.

To investigate the relationship between the electrode and graphene for the voltage generation, we performed four sets of experiments with deionized (DI) water. First, we measured the electrical response of samples in the absence of graphene. In these cases, the devices were connected to an external resistance of 1 k Ω to mimic that of graphene (type-1 and type-2). The results are shown in Figures 2(a) and 2(b); without graphene, there were no noticeable electric responses (only fluctuations at the noise level) before and after switching the water flow on/off at a velocity of 30 mm/s for three repetitions of 30 s. The signal-to-noise ratio (SNR) was less than 5.

$$\text{SNR} = 20 \log_{10}(V_{\text{sig}}/V_{\text{noise}}), \quad (1)$$

where V_{sig} denotes the voltage generated with fluid flow and V_{noise} denotes the voltage generated without fluid flow.

The Rose criterion states that an SNR of at least 5 is needed to distinguish signal from noise with 100% certainty.²⁰ Next, we designed an experimental configuration similar to the one in a previous study,¹⁷ so that the electrodes could be exposed to the flow (type-3). In this case, the voltage increased sharply to 0.21 mV as soon as the flow was switched on, but then subsequently dropped gradually with large fluctuations, as shown in Figure 2(c). Once the flow was turned off, the voltage gradually returned to the resting potential. In the fourth experimental configuration, we measured the electrical response from monolayered graphene samples (type-4) of 5 \times 5 mm² in water flow, where the electrodes were completely separated from interacting with the solutions. Compared with the other samples, the flow-induced voltage generation was distinctly different and appeared in repeatable patterns, as shown in Figure 2(d). When DI water began to flow on the graphene at a velocity of 30 mm/s, the open-circuit voltage reached 0.23 mV and then decreased gradually.

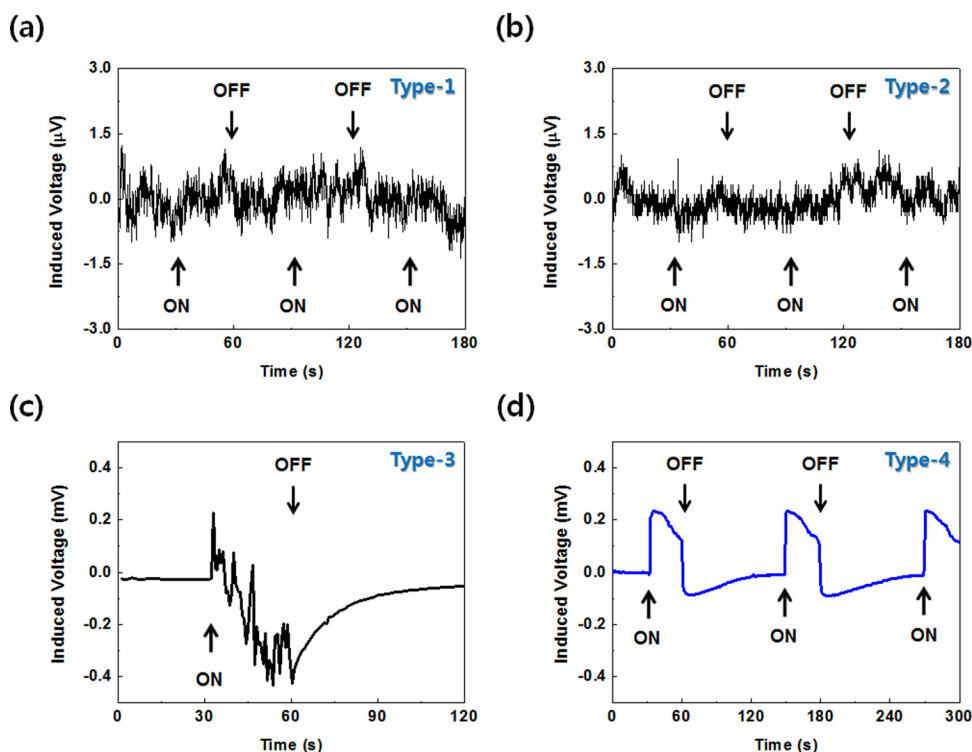


FIG. 2. Voltage response of four kinds of samples to a uniform flow at a fixed velocity. (a) Voltage signal produced in the sample (type-1) for which the electrodes are not exposed to flow. (b) Voltage signal produced in the sample (type-2) for which the electrodes are exposed to flow. (c) Voltage signal produced in the graphene sample (type-3) for which the electrodes are exposed. (d) Voltage signal produced in the graphene sample of $5 \times 5 \text{ mm}^2$ with the electrodes are not exposed to flow (type-4).

When the flow stopped, the voltage dropped to a negative peak of -0.09 mV and then returned to zero. This experimental result clearly indicates that the flow-induced voltage was due to an intrinsic interaction between graphene and the flowing liquid, despite flowing non-ionic DI water.

Next, to investigate the effect of electrode alignment with respect to flow direction, two samples with the electrodes aligned perpendicular (type-4) or parallel (type-5) to the flow direction were prepared. Figure 3(a) shows the measured voltages according to electrode alignment at the same velocity with DI water. Previous studies have reported that flow-induced voltage was only generated in devices with the electrodes aligned parallel to the flow direction, while no voltage was generated when the electrodes were perpendicular to the flow.^{3,16} In our experiments, however, initial voltage was generated even when the electrodes were perpendicular to the flow. Under the same flow velocity, the detected initial voltages were 0.6 and 2.68 mV for the perpendicular and parallel configurations, respectively. Thus, we elucidated the voltage generation mechanism of perpendicular (type-4) electrodes in non-ionic liquids.

Interestingly, when the flow direction was reversed, the generated voltage did not change sign when the electrodes were aligned perpendicular to the flow. On the contrary, a sign change occurred when the electrodes were aligned parallel to the flow. These phenomena are closely related to the phonon-dragging model.¹⁴ Dragging of ions on the surface of graphene may be related to flow-induced voltage, to some extent; however, this is not always the case. In the present experiments, no salt was added, and the pH was approximately 5–7, meaning that approximately only 1 in 10^7 – 10^9 water molecules was a hydronium or hydroxide ion. Considering these results, it is likely that the previously suggested streaming potential model that requires ionic species in solution was not the main mechanism in our present experiment.²¹ To explore the effects of flow velocity over graphene on voltage generation, we measured the electrical signal change as a function of flow velocity. In our study, the flow-induced voltage was proportional to the flow velocity with a non-linear relationship.

To gain detailed insight into the mechanism responsible for voltage generation with graphene in a microfluidic

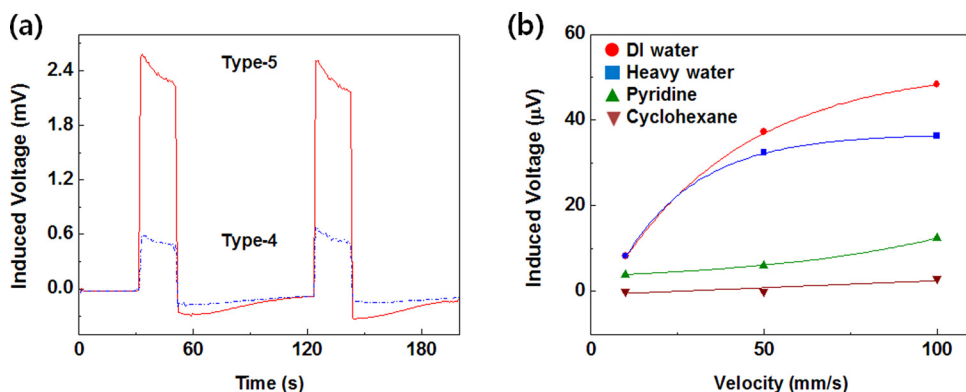


FIG. 3. (a) Voltage response of two kinds of samples (type-4: blue line, type-5: red line). (b) Variation in the flow-induced voltage with polarity and viscosity of liquid.

TABLE I. Summary of experiment results.

	DI water (H ₂ O)	Heavy water (D ₂ O)	Pyridine (C ₅ H ₅ N)	Cyclohexane (C ₆ H ₁₂)
Polarity	Polar protic	Polar protic	Polar aprotic	Non polar
Viscosity (mPa·s)	0.9	1.25	0.88	0.98
Induced voltage (μ V)	48.2	36.3	12.4	2.9

channel, we varied polarity and viscosity of the flowing liquids systematically in the absence of ions; the experimental results are summarized in Table I. We conducted experiments to determine whether voltage depends on polarity. We chose DI water, pyridine, and cyclohexane as solvents to systematically lower the polarity of the flowing liquid, as indicated in Figure 3(b). These solvents were chosen because their viscosities are similar at room temperature (DI water: 0.9 mPa·s; pyridine: 0.88 mPa·s; and cyclohexane: 0.98 mPa·s) and because they differ significantly in their polarity characteristics (protic polar vs. aprotic polar vs. non-polar). Previous studies suggested that the magnitude of the voltage depended on the ionic conductance of the liquid.^{3–11,14–17} However, despite the absence of ions, we observed flow-induced voltages in all polar liquids, and the extent of the voltage generated had a strong correlation with the polarity of the liquid. The flow-induced voltages for DI water, pyridine, and cyclohexane were 48.2, 12.4, and 2.9 μ V at a velocity of 100 mm/s, respectively. On the other hand, the flow of non-polar cyclohexane generated negligible voltages even with the highest flow rate used in our experiments. Based on these results, the polarity of the flowing liquid was identified as an important factor in generating electricity in nanofluidic channels, while the surface-ion-hopping mechanism suggested previously is likely not a primary source of voltage generation because we used non-ionic solutions.

To study the viscosity effect, we next conducted experiments with D₂O (heavy water), as shown in Figure 3(b). A previous study investigated the effect of viscosity using water–glycerol mixtures (88:12 and 75:25) instead of pure water; however, the latter modification also changed the average polarity of the solution, not just the viscosity.³ Thus, to examine the influence of viscosity separately from the polarity effect, we compared H₂O (DI water) vs. D₂O, because H₂O and D₂O have nearly the same polarities but differ in viscosity by 25%. We expected that the increased viscosity would generate less flow-induced voltage, possibly due to a lower degree of momentum transfer from the flowing liquid to graphene. The induced voltage indeed decreased substantially by about 75%, from 48.2 to 36.3 μ V, when the viscosity was increased from 0.9 mPa·s (DI water) to 1.25 mPa·s (heavy water) at a flow velocity of 100 mm/s, thereby confirming a significant viscosity effect.

The surface-ion-hopping mechanism does not explain our observations, because non-ionic solutions induced significant voltages in our experiments. Streaming potential arguments would also require the accumulation of counterions in a thin layer at the solid-liquid interface, which is inapplicable here. On the other hand, various polar liquids, including DI water, are known to form “ordered” structures near hydrophobic interfaces.²² These ordered arrays of dipolar liquid

molecules adjacent to graphene can interact with charge carriers in graphene, resulting in charge redistribution or localization, causing a potential difference.¹⁰ Because more polar liquids would cause a larger charge redistribution, the significant solvent polarity dependence of voltages observed in our experiments is also consistent. With the liquid flowing, these localized carriers can also be dragged along with the flow, yielding flow-velocity-dependent electricity when the electrodes are aligned parallel with the flow direction, in a manner similar to the phonon-dragging model of Kral and Shapiro.¹⁴

The fact that initial voltage (i.e., the voltage when the flow was just turned on) was generated even when the electrodes were aligned perpendicular to the flow direction suggests that mechanisms other than dragging are also in operation, because the flow under the perpendicular electrode configuration would not be able to drag the carriers in graphene in the right direction. We note that there are constant, spontaneous fluctuations of graphene at finite temperatures, i.e., rippling behavior.²³ As soon as the liquid starts to flow, the momentum of the flowing liquid is transferred to the graphene and increases the amplitudes of these equilibrium fluctuations. In particular, the enhanced out-of-plane phonon mode can reorganize the structure of interfacial water (or polar) molecules, such that it reestablishes a new nonequilibrium charge distribution in the graphene, which causes instantaneous potential differences even along the direction perpendicular to the flow due to the delocalized nature of such phonon modes. Thus, as the system reaches a steady-state flow after a sudden onset, these enhanced thermal fluctuations of graphene are brought back into equilibrium, and the potential differences disappear. In other words, the voltage eventually stabilizes to its reference value, 0 V, under the perpendicular configuration, as seen in our experiments. We note, however, that this interpretation requires further investigation and experiments to fully explain the mechanism(s) of flow-induced voltage generation in graphene samples.

In conclusion, we designed a new experimental setup that can clarify the mechanism for flow-induced voltage generation with electrodes completely decoupled from the fluid. We observed that a significant voltage was generated as a result of intrinsic flow over graphene in a non-ionic liquid. This investigation is the first demonstration that flow-induced voltage is closely related to polarity and viscosity of the liquid, independently. The initial voltages at the onset of flow (seen for both parallel and perpendicular electrode configurations) appear to have different origins, considering the stabilized voltages at a steady-state flow velocity, which was seen only in the parallel electrode configuration. We suggest that the charge redistributions of graphene due to polar interactions with the flowing fluid and its dragging may be the key sources of voltage generation for graphene samples. Our experimental results suggest some mechanisms related to energy harvesting and further point toward new directions for studies on flow-induced voltage with nanomaterials.

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