

# Harvesting voltage from non-ionic liquid over monolayer graphene

Seung Ho Lee,<sup>1</sup> Wonsuk Jung,<sup>1</sup> Yousung Jung,<sup>2</sup> Soohyun Kim,<sup>1</sup> and Chang-Soo Han<sup>3</sup>

<sup>1</sup>Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea.

<sup>2</sup>Graduate school of EEWS, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea.

<sup>3</sup>School of Mechanical Engineering, Korea University, Seoul, 136-701, South Korea.

[rururu777@kaist.ac.kr](mailto:rururu777@kaist.ac.kr)

## Abstract

Over the past decade, experimental studies and theoretical interpretations have demonstrated that flow-induced voltage can be generated when carbon nanotubes (CNTs) are immersed in a flowing liquid.<sup>1-3</sup> Kral and Shapiro proposed two possible mechanisms for current generation in metallic single-walled carbon nanotubes (m-SWCNT).<sup>1</sup> The experimental results of Sood *et al.*,<sup>2</sup> were the first report of voltage generation using SWCNT film. They reported that the induced voltage was dependent on the flow velocity, ion concentration, and the electrode alignment with respect to the flow direction. Similarly, it has been reported that multi-walled carbon nanotubes (MWCNTs) highly aligned to the flow direction can produce a higher voltage than non-aligned SWCNTs.<sup>3</sup> Two recent studies on energy harvesting from liquid flow on graphene reported contradictory conclusions.<sup>4,5</sup> 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  $\sim 25$  mV in 0.6 M HCl flowing solution.<sup>4</sup> 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.<sup>5</sup> All of the previous studies employed samples whose electrodes were aligned parallel to the liquid flow and only ionic solutions. Here, we investigated the influence of graphene on voltage generation with new samples, which were aligned perpendicular to liquid flow, using non-ionic liquid.

In this work, electrodes (Au: 40nm, Cr: 10nm) were fabricated by the standard technique of photolithography on glass wafers. Monolayer graphene was synthesized on 70- $\mu\text{m}$  Cu foil inside a chemical vapor deposition (CVD) chamber, as reported previously.<sup>6</sup> We confirmed that the graphene was a monolayer using Raman spectroscopy in Figure 1(a). The intensity ratio of the G and 2D peaks was 2.5–3, indicating monolayer graphene.<sup>7</sup> PDMS block was sealed to the glass surface to complete the microfluidic chip in Figure 1(b). The photographs in Figure 1(c) show samples used in these experiments. We prepared electrode alignments, parallel and perpendicular to the flow direction (type-1: the graphene sample, whose electrode (aligned perpendicular to the flow) was not exposed to flow; type-2: the graphene sample whose electrode (aligned parallel to flow) was not exposed to flow. A schematic of the experimental layout is depicted in Figure 1c. The syringe, driven by a syringe pump, injected the fluid to immerse the graphene and maintained fluid flow at a well-controlled rate. The flow-induced voltage was measured in real time by a digital multimeter connected to computer.

Figure 2(a) shows the measured voltages according to electrode alignment with various flow speeds of 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.<sup>2</sup> In our experiments, however, initial voltage was generated even when the electrodes were perpendicular to the flow. Under the same flow velocity of 100 mm/s, the detected initial voltage (0.6 mV) for the perpendicular alignment was about four times lower than that of the parallel alignment (2.68 mV). At the velocity of 30 mm/s, the flow-induced voltage was appeared in repeatable patterns in Figure 2(b). Thus, we elucidated the voltage generation mechanism of perpendicular (type-2) electrodes in non-ionic liquids.

We systematically varied several experimental parameters to investigate the mechanism of the observed flow-induced voltage: the effects of flow velocity exposed area of graphene, liquid viscosity, and liquid polarity. First, to explore the effects of flow velocity over graphene on voltage production, we measured the electric signal change as a function of flow velocity. The raw data for voltage generation as a function of flow velocity, from 10 to 50 mm/s, are shown in Figure 2(c). It can be seen clearly that the flow-induced voltage is proportional to the flow velocity. By plotting flow-induced voltages against flow velocity, a non-linear relationship was obtained, as shown in Figure 2(d).

To further analyze the mechanism of voltage generation, we conducted experiments with various exposed areas (2–30 mm<sup>2</sup>). As we increased the exposed area of graphene from 2 to 30 mm<sup>2</sup>, the flow-induced voltage change also increased, as shown in Figure 3(a). As larger areas of graphene were exposed to the electrolytic solutions, the amplitude of the wave increased, due to the momentum of the flowing water in the graphene.

To gain detailed insights into the mechanism responsible for voltage generation with graphene in a microfluidic channel, we varied the viscosity and polarity of the flowing liquids systematically without ions. We conducted experiments to determine whether voltage depends on viscosity; we conducted experiments with D<sub>2</sub>O (heavy water), as shown in Figure 3(b). A previous study<sup>2</sup> investigated the effect of viscosity using water-glycerol mixtures (88:12, 75:25) instead of pure water, however the latter modification also changed the average polarity of the solution. So, to examine the effect of viscosity separately from a polarity effect, we compared H<sub>2</sub>O (DI water) vs. D<sub>2</sub>O since H<sub>2</sub>O vs. D<sub>2</sub>O have nearly the same polarities but differ in viscosity by 25%. The induced voltage decreased substantially by about 70 %, from 0.6 mV to 0.19 mV, when we increased the viscosity from 0.9 mPa·s (DI water) to 1.25 mPa·s (heavy water) at a flow velocity of 100 mm/s. And we found similar pattern in experiments with water-glycerol mixtures in Figure 3(c). To study polarity effect next, we chose DI water, pyridine, and cyclohexane as solvent to systematically lower the polarity of the flowing liquid in Figure 3(d). These solvents were chosen since the viscosities of these solvents are similar at room temperature (DI water: 0.9 mPa·s, pyridine: 0.88 mPa·s, cyclohexane: 0.98 mPa·s) but differ in their polarity character significantly (protic polar vs. aprotic polar vs. non-polar). Previous studies<sup>1-5</sup> suggested that the magnitude of the voltage depended on the ionic conductance of the liquid. 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 0.6, 0.16, and 0.03 mV, respectively. Based on these results, the polarity of the flowing liquid was identified as an important factor in generating electricity in nanofluidic channels.

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. Based on these measurements, we suggest that the polarity of the fluid is a significant factor in determining the extent of the voltage generated, and the major mechanism is explained via instantaneous potential differences induced in the graphene due to an interaction with polar liquids as well as the momentum transferred from the flowing liquid to graphene. Our experimental results not only reveal mechanisms related to energy harvesting but also point toward new directions for studies on flow-induced voltage with nanomaterials.

## References

- [1] Kral, P.; Shapiro, M. *Phys. Rev. Lett.* (2001), 86, 131-134.
- [2] Ghosh, S.; Sood, A. K.; Kumar, N. *Science* (2003), 299, 1042-1044.
- [3] Liu, J.; Dai, L.; Baur, J. W. *J. Appl. Phys.* (2007), 101, 064312.
- [4] Dhiman, P. et al., *Nano Lett.* (2011), 11, 3123-3127.
- [5] Yin, J.; Zhang, Z.; Li, X.; Zhou, J.; Guo, W. *Nano Lett.* (2012), 12, 1736-1741.
- [6] Reina, A. et al., *Nano Lett.* **2009**, 9, 30.
- [7] Gupta, A.; Chen, G.; Joshi, P.; Tadigadapa, S.; Eklund, P. C. *Nano Lett.* (2006), 6, 2667-2673.

**Figure**

