

# Energy Harvesting from the Mixture of Water and Ethanol Flowing through Three-Dimensional Graphene Foam

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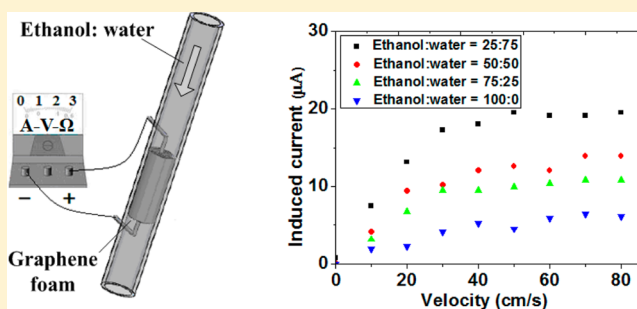
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## S Supporting Information

**ABSTRACT:** In this work, the electrical conductance and induced current of three-dimensional graphene foam (GF) are investigated when the mixture of water and ethanol flows through it. When different mixing ratios of ethanol:water (ethanol:water = 25:75, 50:50, 75:25, and 100:0 by volume) flow through the GFs, their electrical conductance is almost the same as that of the original GF. Meanwhile, the induced current can be obtained when the mixture flows through the GF. The direction of induced current depends on that of the flow of the mixture, the value of induced current has no dependence on the flow direction of the mixture but is closely related to the flow velocity and polarity of the mixture. The mechanism of the induced electricity is discussed, which is attributed to the coupling of flowing solution molecules with the charge carriers of graphene at the solid/liquid interface. These results indicate that GFs have a bright potential application in realizing the self-powered function of nano/micro electromechanical systems (N/MEMS) in many special environments.



## 1. INTRODUCTION

Harvesting energy from the ambient environment directly is one of the most promising and effective approaches for powering nano/micro electromechanical systems (N/MEMS), including ultrasensitive chemical sensors, implantable biosensors, portable/wearable personal electronics, and even remote and mobile environmental sensors.<sup>1,2</sup> Carbon nanomaterials, which are responsible for the conversion of some ambient energy into electrical energy directly, have attracted much attention recently.<sup>3–7</sup> It has been demonstrated that the flow of polar liquids over carbon nanotubes (CNTs) can generate a net potential difference and associated electric current in the nanotubes along the flow direction.<sup>8–10</sup> The induced voltage increases with flow velocity to a saturated value that depends on the ionic conductivity and the polar nature of liquids.

Graphene, a two-dimensional crystal with carbon atoms arranged in a hexagonal structure, has attracted immense interest since it was experimentally discovered.<sup>11–15</sup> Can energy also be harvested when liquids flow over graphene? What may affect the output power? Recently, different research groups have performed related research. In 2011, it was reported that a small piece of graphene sheet about  $30 \times 16 \mu\text{m}^2$  immersed in flowing water with 0.6 M hydrochloric acid can produce voltage of  $\sim 20$  mV.<sup>16</sup> In 2013, Lee et al. reported that voltage generation could be induced in nonionic liquids over

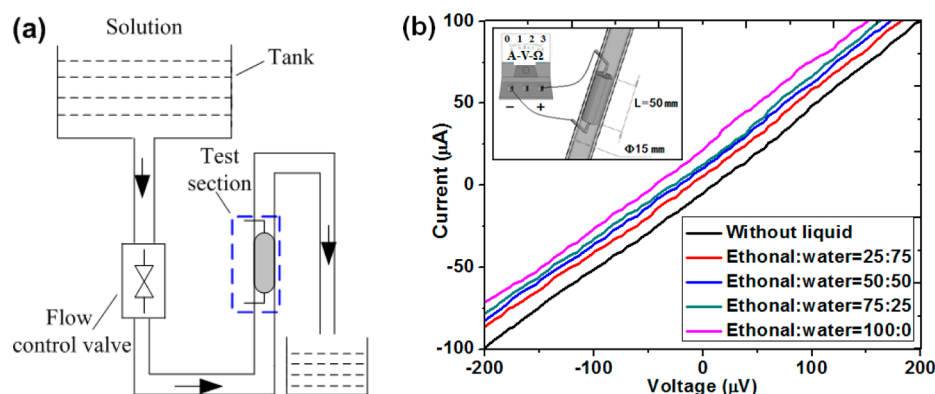
monolayer graphene.<sup>17</sup> Recently, we have reported that electricity can be induced when pure water flows through three-dimensional graphene foam (GF).<sup>18</sup> As a three-dimensional structure, GFs can make full use of specific surface area. Besides, the high quality of the graphene sheets and their perfect connection in GFs give the material excellent characteristics, e.g., outstanding electrical and mechanical properties, etc.

In this paper, we designed a new experiment, in which water is replaced by mixtures of water and ethanol with different volume ratios, which are ethanol:water = 25:75, 50:50, 75:25, and 100:0. The electrical conductance and induced current of GFs were investigated when the mixtures flowed through them. For different mixing ratios, the current–voltage ( $I$ – $V$ ) curves were almost parallel to each other, indicating that the electrical conductivities of GFs were the same. Take the volume mixing ratio of ethanol:water = 25:75 as an example: when the mixture flowed through GF, electricity can be induced. The direction of induced current depends on that of the flow of the mixture, the value of induced current has no dependence on the flow direction of the mixture but is closely related to the flow velocity and polarity of the mixture. The mechanism was

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**Figure 1.** (a) The schematic layout of the flow test facility. (b) The current–voltage characteristics of GFs when the mixtures with different ratios (ethanol:water = 25:75, 50:50, 75:25, and 100:0 by volume) flow through.

studied and attributed to the coupling of solution molecules with the carriers of graphene at the solid/liquid interface.

## 2. EXPERIMENT SECTION

GFs were synthesized on a scaffold of porous nickel ( $5 \times 5 \times 1 \text{ cm}^3$ ) by chemical vapor deposition (CVD).<sup>19</sup> First, we rolled up the porous nickel and put it on a half-round quartz tube, then inserted it into the horizontal tube furnace ( $\sim 32 \text{ mm}$  inner diameter), which was used as the sample growth chamber (Supporting Information, Figure S1a). At  $\sim 1000^\circ\text{C}$  under ambient pressure, carbon atoms were deposited on the nickel foam through  $\text{CH}_4$  decomposition. After growing for about 10 min, a continuous GF formed as a macroscopic structure, and there were extremely thin graphene sheets outside the porous nickel. The graphene sheets spread onto the entire surface of porous nickel and there were no physical breaks in the network. To make sure that the scaffold of porous nickel could be put into the pipe exactly and most of the solution molecules flow through the pores, it was coiled closely into a roll ( $\Phi 15 \times 50 \text{ mm}^2$ ) along the sidelines.<sup>18</sup>

Raman spectroscopy is one of the powerful and convenient tools to characterize carbon nanomaterial, such as CNT and graphene.<sup>20–22</sup> By using the laser excitation of  $\sim 514 \text{ nm}$  of an argon ion laser, the Raman spectra of our samples were collected. To avoid damage to the samples, the laser power was set to be less than 1 mW. An  $\sim 1 \mu\text{m}$  laser spot can be obtained with the application of a  $100\times$  objective lens with a numerical aperture of 0.90.<sup>7</sup> From the intensity ratio of G and 2D modes of the as-grown GF, it can be concluded that the walls of the GF are composed of monolayer to few-layer graphene sheets (Supporting Information, Figure S2).

To measure the  $I$ – $V$  characteristics and induced currents of GFs, we designed a test facility, which was schematically shown in Figure 1a. A long hollow tube was connected to a flow control valve and an overhead tank. By adjusting the height of the flow control valve and the overhead tank, the flow velocity of solution was varied. We attached two metal wires with insulating skin to both ends of the GF roll, and then the GF roll was inserted into the test tube. Through controlling the flow velocity and changing the mixing ratios of solution, which are water:ethanol = 25:75, 50:50, 75:25, and 100:0 by volume, the electrical conductance and induced currents of GFs were measured by a semiconductor characterization system called Keithley 4200-SCS (voltage resolution  $\sim 1 \mu\text{V}$ ).

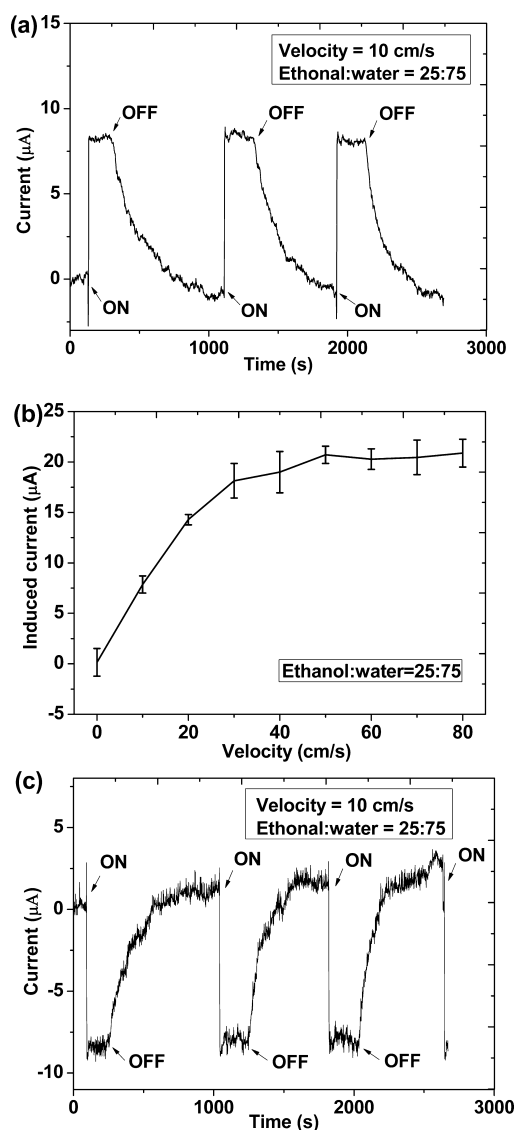
## 3. RESULTS AND DISCUSSION

The electrical conductivity and induced currents of GFs have been investigated when the mixtures flow through. As shown in Figure 1b, for a given mixing ratio, the  $I$ – $V$  curve can be well fitted by using a linear function. Meanwhile, for different mixing ratios, all the  $I$ – $V$  curves are almost parallel to each other, indicating that the electrical conductivity has no change. Furthermore, we can calculate the electrical conductance correspondingly by  $\delta = \Delta I / \Delta V$  ( $I$  and  $V$  are the induced current and voltage, respectively), which is  $\sim 0.5 \text{ S}$ .

We have taken the volume mixing ratio of ethanol:water = 25:75 as an example, and carried out the electrical measurements of our sample in the mode of voltage bias. As shown in Figure 2a, a current of  $\sim 8 \mu\text{A}$  was induced when the bias voltage was set as  $0 \mu\text{V}$  and the flow velocity of solution was  $10 \text{ cm/s}$ ; the character was very repeatable. It was found that the induced current was closely related to the flow velocity of solution, which can be inferred from Figure 2b. When the mixture of water and ethanol flowed in the GFs, the polar molecules of solution would couple with free charge carriers of graphene at the interface. Because of the friction at the solid/liquid interface, continuous coupling and separation happened between the polar molecules and free charge carriers, which led to a nonlinear relationship between the drift velocity of free charge carriers and the bulk flow velocity. The linear velocity of solution ( $v$ ) can be calculated by the following equation:

$$v = V_i / \Delta t S \quad (1)$$

where  $V_i$  is the volume of solution flowing into the can during the time interval  $\Delta t$ , and  $S$  is the flow cross-sectional area of solution in the pipe, which can be calculated by  $\pi r^2$  ( $r$  is the inner radius of the pipe). The induced current is nearly  $0 \mu\text{A}$  when the flow velocity of solution is  $0 \text{ cm/s}$ . In the range of flow velocity of  $0$  to  $60 \text{ cm/s}$ , the induced current becomes larger with the increase of flow velocity, and shows nonlinear dependence on the flow velocity of the solution. For example, when the flow velocity is  $10 \text{ cm/s}$ , the induced current is  $\sim 8 \mu\text{A}$ . The induced current becomes  $\sim 14 \mu\text{A}$  when the flow velocity is set as  $20 \text{ cm/s}$ . However, once the flow velocity exceeds  $60 \text{ cm/s}$ , the induced current tends to a saturated value of  $\sim 20 \mu\text{A}$ . To make sure of the effect of the direction of induced current, a control experiment has been done, in which the flow direction of solution was reversed. In Figure 2c, it is obvious that the induced current goes in the opposite direction, indicating that the direction of induced current is dominated by the flow direction of solution. This means that the induced

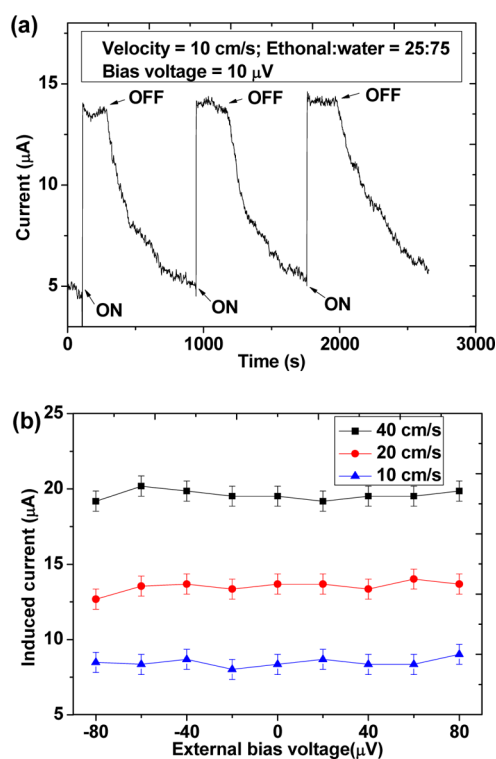


**Figure 2.** (a) The output current when the flow velocity of the mixture (ethanol:water = 25:75 by volume) is 10 cm/s and bias voltage is 0  $\mu\text{V}$ . (b) The variation of induced current in the range of velocity of 0 to 80 cm/s. (c) The output current when the flow velocity and bias voltage are identical with part a but the flow direction is opposite.

current is positive when the solution flows from positive terminal to GND. In contrast, when the solution flows from GND to the positive terminal, the induced current becomes negative. Meanwhile, the induced current measured is very repeatable.

To further explore the relationship between the bias voltage and the induced current, the induced currents have been measured at different bias voltages, which are displayed in Figure 3. In Figure 3a, the induced current was  $\sim 8 \mu\text{A}$  when the bias voltage was defined at 10  $\mu\text{V}$  and the flow velocity of solution was 10 cm/s. From Figure 3b, it can be seen that the induced current has no obvious change when the flow velocity of solution was defined at a certain value despite the bias voltage varying in the negative and positive range. Hence the induced current is independent of the external bias voltage.

As shown in Figure 4a, for the volume mixing ratio of ethanol:water = 25:75, when the flow velocity is  $\geq 60$  cm/s, the



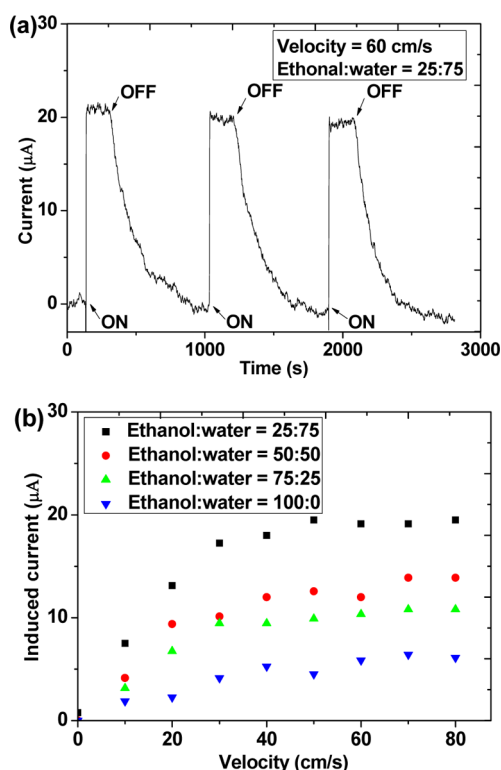
**Figure 3.** (a) The output current when the flow velocity of solution (ethanol:water = 25:75 by volume) is 10 cm/s and bias voltage is 10  $\mu\text{V}$ . (b) The changing trends of induced currents in the negative and positive range of bias voltage when the flow velocity of the mixture (ethanol:water = 25:75 by volume) is 10, 20, and 40 cm/s, respectively.

electrical power reaches the maximum, which can be estimated by the equation:

$$P = I^2 R \quad (2)$$

where  $P$  is the electrical power, and  $R$  ( $1/\delta$ ) is the inner resistance, which is  $\sim 2 \Omega$ . As the flow velocity of the solution increases, the value of  $P$  becomes larger in the range of 0 to 60 cm/s, and finally arrives at a value of  $\sim 0.8$  nW when the flow velocity reaches and exceeds 60 cm/s. We are trying to expand the electrical power by reducing the diameters of the holes in GFs in follow-up experiments.

To investigate the influence of solution polarity on the induced current, we have changed the volume mixing ratio of the solution to ethanol:water = 50:50, 75:25, and 100:0 in turn. According to the empirical formula for calculating the polarity of the mixed solution, we can obtain the polarities of mixed solutions (ethanol:water = 25:75, 50:50, 75:25, and 100:0 by volume), which are 8.73, 7.25, 5.79, and 4.3, respectively. They reflect the obvious change of solution polarity with the increase of ethanol volume percentage in the mixture. To explore much more, the induced current was compared to the polarity in a more quantitative way in Table 1, from which it can be easily concluded that the saturated value of the induced current becomes smaller and smaller as the volume percentage of ethanol in the mixture increases, as shown in Figure 4b. The reason is studied and discussed, and is mainly attributed to the change of solution polarity. A previous study has investigated the effect of viscosity by using water–glycerol mixtures (88:12 and 75:25).<sup>2</sup> However, in our experiment, the viscosities of water and ethanol at room temperature are similar and the



**Figure 4.** (a) The induced current when the flow velocity of solution (ethanol:water = 25:75 by volume) is 60 cm/s and external bias voltage is 0  $\mu\text{V}$ . (b) The variation of induced currents as the flow velocity changes in the range of 0 to 80 cm/s when the bias voltage is 0  $\mu\text{V}$  and the mixing ratios of solution are ethanol:water = 25:75, 50:50, 75:25, and 100:0 by volume, respectively.

**Table 1. Comparison of Measuring Characters to Different Mixing Ratios of Solution**

ethanol:water (by vol)	25:75	50:50	75:25	100:0
polarity	8.73	7.25	5.79	4.3
satd current ( $\mu\text{A}$ )	$\sim 20$	$\sim 14$	$\sim 9$	$\sim 5$

viscosities of their mixtures have little difference, so the viscosity effect can be ignored. We can finally confirm that the polarity of the solution is a significant influence factor of the induced current.

What is the mechanism of the interesting observations? The interpretation of electrode–solution interaction<sup>6</sup> cannot explain what has been observed in our experiment, because the measuring results when the junctions were coated with PMMA are almost the same as Figure 2a. The streaming potential model<sup>23,24</sup> is also not applicable since it shows a linear response to the changing flow rate of water, while we observe a nonlinear dependence. By using the mutual iterative method of density functional theory (DFT) and molecular dynamics (MD), it has been demonstrated that interactions between the water dipoles chains and charge carriers in a single-wall CNT can result in charge redistributions, causing a voltage difference of several millivolts between the two ends of the tube.<sup>25,26</sup> As a single layer of  $\text{sp}^2$ -bonded carbon atoms, graphene has a similar structure as the tube wall of a single-wall CNT, so when the mixed solution flows in GFs, polar solution molecules will also couple with free charge carriers of graphene at the solid/liquid interface. Free charge carriers are dragged along the flow direction, forming an induced current. Free charge carriers

move quicker as the flow velocity increases, leading to the increase of induced current. Because of the friction at the solid/liquid interface, continuous coupling and separation will happen between the polar molecules and free charge carriers, which lead to a nonlinear relationship between the drift velocity of free charge carriers and the bulk flow velocity. When the polar solution flows along the opposite direction, the induced current is reversed. However, the absolute values of induced currents are almost equal when the flow velocity remains constant in spite of the flow direction changes. With the increase of ethanol volume percentage in the mixture, the solution polarity decreases, which will cause the fall of induced current for a given flow velocity.

## 4. CONCLUSIONS

In conclusion, GFs were synthesized by CVD. The electrical conductance and induced currents of GFs were investigated when the mixture of water and ethanol flowed through them. The electrical conductivity of GF had no change as the mixing ratios of ethanol and water differed. When the mixture flowed through GF, electricity can be induced. The flow of mixture determined the direction of the induced current, but had no effect on the value of induced current. The induced current was found to be nonlinearly dependent on the flow velocity of solution in the range of 0 to 60 cm/s. When the flow velocity exceeded 60 cm/s, the induced current tended to be a saturated value. The polarity of the solution was found to have positive correlation with the induced current. The mechanism was studied and attributed to the coupling of flowing solution molecules with the charge carriers of graphene at the solid/liquid interface. The experimental results indicated that GFs have a bright application prospect in realizing the self-powered function of N/MEMS. Besides, the unique network structure of GF can enable many other applications, including elastic and flexible conductors, high-performance electrically conductive polymer composites, electrode materials for lithium ion batteries and supercapacitors, etc.

## ■ ASSOCIATED CONTENT

### Supporting Information

Synthesis of three-dimensional graphene foam; SEM of porous nickel and three-dimensional graphene foam; and Raman spectra of three-dimensional graphene foam. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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