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Self-powered wearable graphene fiber for information expression

Yuan Liang[a], Fei Zhao[a], Zhihua Cheng[a], Qinhan Zhou[a], Huibo Shao[a,*], Lan Jiang[b], Liangti Qu[a,*]

[a] Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China
[b] Laser Micro-/Nano-Fabrication Laboratory, Beijing Institute of Technology, Beijing 100081, PR China

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ABSTRACT

With the fast development of wearable electronics, portable energy generation devices are attracting our considerable attention. Among them, the wearable self-powered system spontaneously harvesting energy from the environment will be much needed. Herein, a high-performance graphene fiber power generator (GF-Pg) is produced based on graphene oxide (GO) fiber. The GF-Pg has highly oriented GO sheets assembled within the fiber, which provide favorable channels for efficient ion transport and thus harvests energy from the moisture. A single fiber generator unit with a length of less than 1 mm and a diameter of 80 μm was able to supply a voltage output of 355 mV in response to the humidity variation, which could be enhanced to 1.3 V by simply increasing the number of device units. Impressively, this moisture-enabled self-powered fiber could be integrated into flexible textiles to realize an information storage/expression based on the breath activated electronic labels of GF-Pg, demonstrating the promising applications in wearable electronics.

1. Introduction

The boom of mobile electronics rises up the human reliance on portable power sources. Meeting this requirement, the burgeoning wearable energy generators have recently been attracting the tremendous attention as a promising power supply for future pocket equipment [1–5]. Advance has been made to develop the power generators (Pg) that can convert environmental energy including thermal energy [4,6–8], solar energy [9–13] and mechanical energy [14–20] to the electric power. Unlike the conventional planar devices based on flexible substrates [21–23], fibriform devices can be directly woven into textile fabrics for wearable electronics [24–30].

Recently, we have demonstrated the moisture-electric energy transformation (MEET) process to achieve a highly efficient energy harvesting from environment [31,32], which stands for a new type of power resource and opens new opportunities for the electric power generation. The MEET mechanism is based on the hydration of functional materials (e.g., graphene oxide, GO) with gradient distributed ionizable groups, in which the free ions were released by water molecule triggered ionization. The migration of free ions driven by the concentration gradient induced the generation of voltage and current. The hydroelectric power generation from MEET process is directly related to the hydrophilicity, permeability and ionic conductivity of functional materials.

GO nanosheets with plenty of oxygen-related groups can be assembled into the fibers through the highly oriented arrangement of GO sheets [25,33–36]. The ordered inter-layer channels along the fiber largely facilitate the mass transportation as demonstrated by a fiber supercapacitor [36]. Herein, we report a graphene fiber power generator (GF-Pg) for harvesting energy from environmental moisture. The single GF-Pg with a length of less than 1 mm and a diameter of only 80 μm was able to supply a high voltage output of ca. 0.4 V upon the variation of environmental relative humidity (ΔRH), which could be enhanced to 1.3 V by simply increasing the number of device units. Moreover, this moisture-enabled self-powered fiber could be integrated into flexible textiles to realize an information storage/expression based on the breath activated electronic labels of GF-Pg, exhibiting the promising applications in wearable electronics.

2. Experimental section

The precursor of GO fiber (GOF) was prepared by a large-scale wet-spinning method [25,35,36], in which the GO gel with concentration of 18 mg mL^{-1} is directly injected into a saturated KCl/methanol solution (see Supplementary information for details). The obtained precursor was dehydrated under applied pull force to contribute the aligned arrangement of GO nanosheets along the fiber (Fig. 1a). GF-Pg was fabricated by well-controlled region-selective laser irradiation along the GOF to form the reduced GO (RGO) electrodes in series as illustrated in our previous work (Fig. 1b and Fig. S1) [36]. The region along GO fiber exposed to laser scan was selectively reduced into RGO. The final

* Corresponding author.
E-mail addresses: hbs@bit.edu.cn (H. Shao), lqu@bit.edu.cn (L. Qu).

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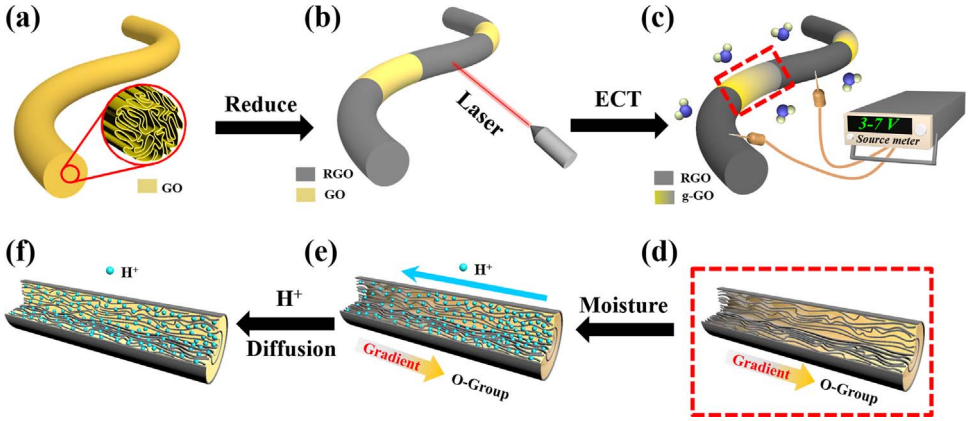

Fig. 1. Schematic illustration of the fabrication of a GF-Pg. (a) The GO fiber composed by aligned GO sheets. (b) Prepare the RGO-GO structure by laser selective writing. (c) Electrochemical treatment process: constant bias voltages (3–7 V) are applied between the adjacent RGO parts in high relative humidity. (d) Gradient distribution of oxygen-containing groups in functional part of GF-Pg after ECT process. (e, f) The hydrogen ions were ionized under moisture, and the hydrogen ions diffused from the oxidized end to the reduced end until reaching the final equilibrium.

graphene fiber with alternative distribution of RGO and GO is denoted as ROR-GF. The concentration of oxygen-related groups in GO region was regulated to be gradient (named as gradient oxygen-containing GO region, i.e. *g*-GO region) through an electrochemical treatment process (ECT) we developed recently (Fig. 1d) [31,32]. The ECT induced *g*-GO region serves as functional part. During ECT, a constant bias in an appropriate scope (3–7 V) is applied on the device unit sealed in a closed container under high environmental RH (Fig. 1c). The RH in the container is adjusted by dry nitrogen and the flow of water moisture (Fig. S2). Driving by the voltage, the negative-electrode-contacting end and the positive-electrode-contacting end of the fiber are partially reduced and slightly oxidized, respectively (Fig. 1d). After GO part absorbed water, the hydrogen ion (H^+) was ionized from the oxygen-related groups and directly transported from the oxidized end to the reduced end drived by the concentration gradients (Fig. 1e and Fig. 1f). The current and voltage outputs could be detected after GF-Pg was connected into an external circuit.

3. Results and discussion

Just as the GO fiber precursor, the GF-Pg presents good mechanical strength (Fig. S3) and excellent flexibility (Fig. 2a). Fig. 2b displays the alternated bright and black sections on the GF-Pg corresponding to the RGO and *g*-GO regions, respectively. The GO sheets were highly aligned directionally along the fiber axis both on the surface and internal structures of the fiber (Fig. 2c, Fig. S4 and S5). The inner layer-by-layer assembled GO sheets form the favorable inter-layer channels for ion transport (Inset of Fig. 2c and Fig. S5). This well-organized structure was achieved by pulling the fiber at two ends during the drying process to induce the GO sheets aligning along the axial (Fig. S4 and S5). Moreover, the energy dispersive spectroscopy (EDS) directly reflects the gradient distribution of the oxygen component on a highly oriented GF-Pg (Fig. 2d). The surface C/O atomic ratio of *g*-GO is 2:1, 4:1 and 10:1 corresponding to the 1, 2 and 3 positions (Inset of Fig. 2d). Meanwhile, the inner C/O atomic ratio of *g*-GO is consistent with the surface (Fig. S6).

To evaluate the moisture-electric transformation, GF-Pg was connected into an external circuit and exposed to moisture (Insets in Figs. 3a and 3b). Since the available H_2O molecules will effectively trigger the ionization of oxygen-containing functional groups in *g*-GO, the induced voltage and current outputs depended on the environmental RH change. As shown in Figs. 3a and 3b, in a relatively small humidity variation of 10%, the output voltage and current density are 110 mV and 0.19 mA cm^{-2}, respectively. With the increase of the ΔRH=35%, both the voltage and current density augment to 290 mV and 0.46 mA cm^{-2}, which is nine times higher than the output voltage of GO film-based generator [31]. This largely enhanced output power probably benefits from the horizontal ion transmission manner that the ions transfer between the GO channels aligning along the fiber instead of the transverse transmission through the film in which ions cross obstacles of GO layers. Under the ΔRH=65%, voltage and current density can be further raised to 355 mV and 1.06 mA cm^{-2}. The maximum power of one GF-Pg is 37.6 mW/cm^3. The induced power of GF-Pg is apparently dependent on the level of humidity variation. When the GF-Pg was exposed to the moisture, the voltage and current rose rapidly. After the relative humidity decreased, the signals of output went down and reversed (Fig. 3c and 3d) [31]. Fig. 3e shows the cyclic stability of voltage output for a GF-Pg unit. It retains 90% of its initially generated voltage after 200 cycles of humidity alternation (15–50%). Meanwhile, the fiber possesses mechanical flexibility and can be easily bent without damage in structure (Fig. 2a and Fig. S3). As a result, the output voltage of GF-Pg with the bending radius of 2.8 mm still maintained 95% of its initial value after being bent 80° for 1000 times (Fig. 3f). This good mechanical flexibility and reliable power generation of GF-Pg provides the possibility to be embedded into textiles for the wearable devices (Fig. S7).

The moisture-triggered power output can be future improved by connecting device units in series and in parallel manner (Insets of Fig. 3g and Fig. 3h). Four units are simultaneously integrated in one fiber by laser writing for ten seconds and the number of unit in the fiber can be adjusted according to the length of the GOF. Under the ΔRH=65%, the voltage V_1 and the corresponding current density A_1 of one single device unit along the fiber are about 0.35 V and 1.05 mA cm^{-2}, respectively. After two, three and four GF-Pg units are connected in serial, the voltages V_2, V_3 and V_4 can be up to 0.69 V, 1.02 V and 1.32 V, which conform to the series theory (Fig. 3g). The corresponding maximum output of parallel current density A_4 reaches to 3.6 mA cm^{-2} (Fig. 3h). As a result, the output power can be conveniently adjusted through series and parallel connections according to the actual needs in the future.

The difference of output voltages of the GF-Pg units could be related to the information expression. For example, the ROR-GF unit untreated by ECT has an output of 0 mV under the humidity change, which can be considered as the “0” (OFF) status. On the contrary, the ECT treated *g*-ROR unit having a high response voltage can be named “1” (ON) status (Fig. S8a). The elements “0” and “1” form the basic