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Highly Conductive Graphene Paper with Vertically Aligned Reduced Graphene Oxide Sheets Fabricated by Improved Electrospray Deposition Technique

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KEYWORDS: Reduced graphene oxide paper; Electrospray deposition technique; Vertically aligned; High conductivity; Stretchable electronics
ABSTRACT

Because of its notable electrical and mechanical properties, the highly conductive graphene paper has great potential applications in future flexible electronics. In this study, we report a simple and effective method to prepare vertically aligned graphene oxide papers from graphene oxide suspensions by an improved electrospray deposition technique with a moving stage which is controlled by computer. And then, the flexible reduced graphene oxide papers are successfully synthesized after reduction by using hydroiodic acid. The obtained reduced graphene oxide paper has an electrical conductivity as high as 6180 S/m, which is more than one and a half times of the reduced graphene oxide paper film which was fabricated by using the electrospray deposition technique without the moving stage. The experimental results approved for the first time that the degree of alignment of reduced graphene oxide sheets can affect the conductivity of the reduced graphene oxide papers. Further electrochemical measurements for a symmetrical supercapacitor device based on the prepared reduced graphene oxide paper indicate that it has great capacitive performance and electrochemical stability. It exhibited relatively high specific capacitance (174 F g⁻¹) at a current density of 1 A g⁻¹ in 6 M KOH aqueous solution and its capacitance can retain approximately 86% after 1000 cycles. In addition, patterned freestanding reduced graphene oxide papers which have potential applications in many fields such as stretchable electronics and wearable devices also can be fabricated by using this method.
1. INTRODUCTION

Highly conductive graphene-based paper preserve plenty of remarkable properties of graphene, has recently attracted considerable attention due to its potential application in various fields, such as supercapacitors,\textsuperscript{1-3} transparent conductors,\textsuperscript{4,5} and sensors,\textsuperscript{6} etc. Owing to the high melting point of inorganic graphene, fluid assembly is the optimized method to fabricate macroscopic ordered materials. Until now, producing graphene-based paper from graphene oxide (GO) still is an accessible and low-cost approach, since it is suitable for large-scale production and can easily assemble into film by solution processes such as vacuum filtration,\textsuperscript{7,9} spray coating, dip coating,\textsuperscript{4,10} wet spinning,\textsuperscript{11} chemically engineering approach,\textsuperscript{12} or scrape coating method.\textsuperscript{13-14} However, the obtained graphene oxide paper (GOP) is almost an insulator because the GO sheets contain with abundant oxygenated functional groups on their basal plane and edges.\textsuperscript{13,5-16} Therefore, an effective deoxygenating process must be implemented primarily to make the as-prepared insulating GOPs to be conductive. So far many methods for the reduction of GOPs have been studied including high temperature thermal annealing\textsuperscript{4,17} and low temperature chemical reduction.\textsuperscript{5,9,12-14,18-20} And these deoxygenating processes are successful for improving the conductivity of the reduced GOPs (r-GOPs). Among them, some representative works have been cited thousands of times by other authors in scientific publications.\textsuperscript{4,5,9,18-19} However, the properties of r-GOPs are related to not only the properties of reduced GO (r-GO) sheets, but also the arrangement and degree of alignment of r-GO sheets, especially in electrical conductivity. But those assembly methods mentioned above are difficult to obtain freestanding GOPs with highly vertically aligned GO sheets because of the rigid experimental and process conditions.

As a common fluid assembly technique, electrospray/electrospinning deposition (ESD\_spr/ ESD\_spi) has been widely applied in the fabrication of various thin films because of its high precision for properties
control and less material loss.\textsuperscript{21-25} Recently, because it can effectively improve the uniformity of sheets in the sprayed area, graphene or graphene oxide thin films by ESD\textsubscript{spr} method have been reported and used in a variety of applications, such as resistive switching device,\textsuperscript{26} supercapacitor,\textsuperscript{1-2} and super thermal management,\textsuperscript{27} etc. In the ESD\textsubscript{spr} process, a precursor solution feeding through a stainless steel nozzle will be atomized at the tip of the nozzle because of the repulsion forces between charges in the droplets after a high electric potential was applied between the nozzle and substrate. And then, the atomized small droplets deposit on the substrate to form a uniform thin film. So the properties of the deposition film are closely related to the ESD\textsubscript{spr} parameters such as the flow rate of precursor solution, the distance between nozzle and substrate, and the applied potential, etc.\textsuperscript{28} In addition, many studies have demonstrated that the degree of alignment of fibers can be adjusted by changing the relative speed between nozzle and substrate in the ESD\textsubscript{spi} process.\textsuperscript{29-30} Therefore, the freestanding GOPs with highly vertically aligned GO sheets may be fabricated by using the ESD\textsubscript{spr} technology cooperated with a movable substrate.

In this work, we present a more efficient method to prepare vertically aligned GOPs by using an improved ESD\textsubscript{spr} technique with a moving stage which is controlled by computer. After reduction by using hydroiodic acid, the prepared r-GOP film has a higher electrical conductivity more than one and a half times of the r-GOP film which was fabricated by using the ESD method without moving stage. And for all we know, this is the first time to experimentally prove that the arrangement and degree of alignment of r-GO sheets can affect the conductivity of the r-GOP materials. Further electrochemical measurements for a symmetrical supercapacitor device based on the prepared r-GOP films indicate that it has great capacitive performance. In addition, patterned freestanding r-GOPs which have potential applications in stretchable electronics and wearable devices can also be fabricated by using this method.
2. RESULTS AND DISCUSSION

Figure 1. Optical images of (a) GOP with the thickness of 1.2 μm and (b) r-GOP. (c) Optical micrograph of patterned GOP with round holes array. Cross-sectional SEM images of (d) GOP and (e) r-GOP. (f) SEM image of r-GOP (top view).

The obtained GOPs and r-GOPs are flexible and free-standing indicating that the individual sheets within the paper have formed continuous networks to provide mechanical integrity and good structural. Photographs of GOP and r-GOP are shown in Figure 1a and b, respectively. The electrical conductivity of GO sheet has dramatically improved after reduction which makes r-GOP film have a metallic luster in comparison to GOP film, as reported elsewhere.9,31 Furthermore, patterned freestanding GOPs also can be fabricated by using this setup. The patterned films have potential applications in many fields such as stretchable electronics and wearable devices because they have many advantages in mechanical properties.32-33 In order to fabricate the patterned freestanding GOP films, just need to replace the aluminum...
foil with the metal substrate with special architectures. So the electric filed in the spraying zone can be changed which can affect the distribution of sediments. For example, the patterned freestanding GOP with round hole structure as shown in Figure 1c was prepared by using the aluminum plate with round holes array as the collector substrate.

![Figure 2. Schematic illustration of the process for fabricating GOPs (a) the GO sheets in the spraying zone, (b) depositing the GO sheets on the substrate.](image)

In the synthesis process of GOP film as shown in Figure 2, the GO sheets were separated in the spraying zone due to the electric field repulsive force and fell towards to the collector substrate as a result of the action of electric field attractive force and the gravity of solution as shown in Figure 2a. The GO sheets will bend when they get to the collector substrate because of surface contact stress between them if keep the collector substrate still or its lateral speed less than the sheets’ dropping speed. However, once the lateral speed of the collector exceeded the sheets’ dropping speed reach a critical value, the GO sheets will flat on the collector.
substrate as shown schematically in the Figure 2b. This conclusion comes from the basic knowledge of mechanics and has been proved in the previous study. By carefully adjusting the ESD$_{spr}$ parameters such as the flow rate of precursor solution, the distance between nozzle and substrate, and the applied potential, and the moving speed of the platform during ESD, a highly vertically aligned structure can be assembled in GOP as shown in Figure 1d. And the reduced graphene sheets within the r-GOP film have a looser multilayered structure because of the removal of oxygen-containing functional groups and water molecules intercalated in the spacing between the GO sheets as shown in Figure 1e. In addition, the surface of r-GOP still has some protuberant wrinkles and ripples as shown in Figure 1f.

Figure 3. (a) Raman spectra of GOP and r-GOP. (b) Energy dispersive X-ray spectroscopy of (b) GOP and (c) r-GOP.
Figure 4. (a) XPS spectra of GOP and r-GOP. XPS C1s peak of (b) GOP and (c) r-GOP.

In order to illustrate the changes in structure and composition after reduction, the structural information and elemental analyses were investigated by Raman, energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS), respectively. In the Raman spectra of GOP and r-GOP (Figure 3a), they all contain both D and G bands, which corresponding to the breathing modes of sp² atoms and the first-order scattering of the E₂g mode, respectively. After reduction, the G band down-shift to 1582 cm⁻¹ which matched well with that of pristine graphene from 1596 cm⁻¹, and the intensity ratio of two peaks (I_D/I_G) in r-GOP remarkably increased compared to that in GOP which proves the increase of sp² carbon, these all indicating that the GO sheets in GOP were successfully reduced into graphene sheets in r-GOP. In addition, the 2D band (2660
cm$^{-1}$) (Figure S1) is increased after HI acid reduction, further proves the restoration of sp$^2$ carbon in r-GOP films. 9, 35, 42 The increased C/O atomic ratio is another important evidence of the removal of oxygen-containing functional groups of the GO sheets upon reduction. 9 According to the EDS and XPS spectra as shown in Figure 3b-c and Figure 4a, the results present that the sample contains C, O, and I element after HI acid reduction and the C/O atomic ratio is increased to above 5 which is more than twice the value of GOPs. Remove of the oxygen-containing groups in the reduction process also can be proved by the high resolution C1s peaks. As the C1s spectrum of the GOP shown in Figure 4b, it consists of two main components arising from C–C (~284.8 eV) and C–O (~287 eV) groups and two minor components from C=O (~288.3 eV) and O=C-O (~290.3 eV) groups as earlier reports. 5, 9 And the C–C bonds become dominant along with the majority of oxygen-containing groups in GO sheets (C-O groups) are almost removed after HI acid reduction (Figure 4c).
Figure 5. (a) Schematic diagram of simplified model of r-GO sheets and the angle resolved polarized Raman configuration. (b) Polar plot of the angle resolved polarized Raman intensity of G mode of r-GOPs and r-GOP$_{nos}$

Because of the damages on the fine lattice structure of graphene in GO preparation, the r-GOPs have loose multilayered structure and their GO sheets could inevitably form curved structures, as shown in Figure 1e. To quantify and compare the alignment degree of the r-GOPs and r-GOP$_{nos}$, we measured the angle resolved polarized Raman intensity of the sensitive G band, which is widely used in the characterization of arrangement and alignment degree of GO films.$^{36-37}$ Figure 5a shows the schematic diagram of the simplified model of GO sheets and the angle resolved polarized Raman configuration. The laboratory coordinate (x, y, z) is shown in black vectors with the y-axis and z-axis paralleling and perpendicular to the basal plane/length direction of the r-GOP, respectively. We simplify our models by assuming that the graphene nanosheets of r-GOP are uniformly distributed with an average alignment angle $\alpha$ from the basal plane/length direction. The intensity of a Raman active mode with Raman tensor $R_j$ is calculated by: $I = \sum_j |e_s \cdot R_j \cdot e_L|^2$, where $e_L$ and $e_s$ are the unit electric field vectors of the incident laser and scattered Raman signal, respectively. Raman tensors $R_j$ of the G mode can use that of HOPG and the calculation principle can be found in Ref.$^{38}$ In this work, the incident laser propagates along the x direction and is initially vertically polarized. The laser polarization is then changed continuously through a half-wave plate so that $e_L = (0 \ \cos \theta \ - \sin \theta)$, in which $\theta$ is the angle between laser polarization and y-axis. A polarization analyzer is fixed before the spectrometer to collect only the Raman signal paralleling to the y-axis with $e_s = (0 \ \ 1 \ \ 0)$. Therefore the total Raman intensity of the G mode contributed from both sides of GO films is given by:
\[ I_G(\theta) = \frac{1}{2} e^2 \cos^2 \alpha \{2 + \cos[2(\alpha - \theta)] + \cos[2(\alpha + \theta)]\} \]  

(1)

Obviously, \( I_G \) would reach the maximum (\( I_{\text{max}} \)) and minimum (\( I_{\text{min}} \)) when the electric field vector of the incident laser \( e_l \) is parallel (\( \theta = 0^\circ \) and \( 180^\circ \)) and perpendicular (\( \theta = 90^\circ \) and \( 270^\circ \)) to the basal plane of the GO films, respectively. And their ratio \( I_{\text{max}}/I_{\text{min}} = \cot^2 \alpha \) is monotonically decreasing with \( \alpha \) and thus can intuitively quantify their alignment degree. Therefore, the angle resolved polarized Raman technique can be utilized to compare the alignment degree of the samples we prepared.

The experimental results of r-GOPs and r-GOP\(_{\text{no}}\)s are shown in Figure 5b, the angle (\( \theta \)) between the electric field vector of the incident laser and the basal plane was tuned from \( 0^\circ \) to \( 350^\circ \) with a step of \( 10^\circ \). The intensity of G mode, \( I_G(\theta) \), reached a maximum (\( I_{\text{max}} \)) when the electric field vector of the incident laser was parallel to the basal plane of the r-GOPs and r-GOP\(_{\text{no}}\)s and a minimum (\( I_{\text{min}} \)) when perpendicular to the basal plane. The result of fitting the experimental data by the Equation 1 is indicated by red and blue solid lines in Figure 5b, which is in good agreement with the experimental results. For both r-GOPs and r-GOP\(_{\text{no}}\)s, the experimental \( I_G(\theta) \) decreases gradually when \( \theta \) varies from \( 0^\circ \) to \( 90^\circ \). From the results shown in Figure 5b, the \( I_{\text{max}}/I_{\text{min}} \) is 8.09 in r-GOP which corresponds to the averaged alignment angle to be \( 19.4^\circ \). However, the \( I_{\text{max}}/I_{\text{min}} \) is decreased to 3.69 in r-GOP\(_{\text{no}}\)s which corresponds to a larger angle of \( 27.5^\circ \), that value is slight smaller than the earlier report\(^3^7\) in which the averaged alignment angle is \( 28.3^\circ \) of GO films fabricated by flow-directed filtration method. These above results indicate that microstructural evolution occurred and caused improved alignments during the fabrication process by the improved electrospray deposition technique with a moving stage in this work.
Figure 6. I-V curves at different temperatures of r-GOP.

The properties of materials are closely related to the internal microstructure. Hence we infer that the properties of r-GOP based on highly vertically aligned reduced graphene oxide sheets should have advantages in some respect such as electrical conductivity. In order to verify this, the I-V characteristic of the r-GOP under different temperatures has been measured and displayed in Figure 6. The I-V curves can be well understood by a semiconductor behavior, as the resistance increased with decreasing temperature. To compare the different of the two kinds of samples which were fabricated by using the ESD method with or without moving stage used the same usage amount of GO dispersion, the C/O atomic ratios, the I_D/I_G ratios, film thickness, and volume conductivity were listed in the table 1. It can be seen that the C/O atomic ratios and the I_D/I_G ratios of the six samples are almost identical, which indicate that the reduced GO sheets which formed the r-GOPs have the same fundamental qualities. The thickness of r-GOPs is increased in proportion to the usage amount of GO dispersion.
Interestingly, the thickness of r-GOPs is always smaller than that of r-GOP\textsubscript{no}s under the same usage amount of GO dispersion which was caused by the highly vertically aligned of reduced GO sheets in the r-GOPs. And this can improves the contact of adjacent reduced GO sheets which may easier to the electrons transport in the r-GOP films. As shown in table 1, the volume conductivities of r-GOPs with different thickness just have slight variations, but it is far greater than that of r-GOP\textsubscript{no}s.

**Table 1. Properties comparison of six different kinds of r-GOPs.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Fabrication method</th>
<th>Reductant</th>
<th>C/O atomic ratio (EDS/XPS)</th>
<th>$l_0/l_G$</th>
<th>The usage amount of GO dispersion (ml) /Thickness of film(μm)</th>
<th>$R_s$ (Ω/sq)</th>
<th>$\sigma$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r-GOP\textsubscript{1}</td>
<td>ESD with moving stage</td>
<td>HI</td>
<td>5.60/5.36</td>
<td>1.10</td>
<td>5/0.70=7.1</td>
<td>231</td>
<td>6180</td>
</tr>
<tr>
<td>r-GOP\textsubscript{2}</td>
<td>ESD with moving stage</td>
<td>HI</td>
<td>5.63/5.28</td>
<td>1.08</td>
<td>10/1.20=8.3</td>
<td>140</td>
<td>5950</td>
</tr>
<tr>
<td>r-GOP\textsubscript{3}</td>
<td>ESD with moving stage</td>
<td>HI</td>
<td>5.57/5.23</td>
<td>1.02</td>
<td>20/2.65=7.5</td>
<td>65</td>
<td>5805</td>
</tr>
<tr>
<td>r-GOP\textsubscript{no-1}</td>
<td>ESD without moving stage</td>
<td>HI</td>
<td>5.63/5.32</td>
<td>1.18</td>
<td>5/0.87=5.7</td>
<td>298</td>
<td>3857</td>
</tr>
<tr>
<td>r-GOP\textsubscript{no-2}</td>
<td>ESD without moving stage</td>
<td>HI</td>
<td>5.73/5.11</td>
<td>1.05</td>
<td>10/1.69=5.9</td>
<td>151</td>
<td>3918</td>
</tr>
<tr>
<td>r-GOP\textsubscript{no-3}</td>
<td>ESD without moving stage</td>
<td>HI</td>
<td>5.59/5.40</td>
<td>1.21</td>
<td>20/3.13=6.4</td>
<td>87</td>
<td>3672</td>
</tr>
</tbody>
</table>
Figure 7. The cyclic voltammetry curves recorded in 6 M KOH of r-GOP electrodes at different scan rates. (a) 0.7-μm-thick electrode, (b) 1.2-μm-thick electrode. The galvanostatic charge/discharged curves of r-GOP electrodes at different current densities. (c) 0.7-μm-thick electrode, (d) 1.2-μm-thick electrode.

To further make sure about the favorable characteristics of the r-GOPs, its electrochemical properties were also evaluated on an electrochemical station as the earlier works. In view of the stable structure of the r-GOP films, the symmetrical supercapacitors have been fabricated by used the r-GOP films of different thickness (0.7 and 1.2 μm) as the electrodes directly. The CV curves of two thickness electrodes all show well quasi-rectangular shapes at low scan rates and the shapes were maintained even at the scan rate as high as 200 mV s\(^{-1}\) (Figure 7a and b). This indicates that these two electrodes all show well capacitive
properties and have excellent rate capability. GCD tests were also used to study the properties of the thin-film electrode. The GCD curves of these two electrodes all show triangular shape at different current densities (Figure 7c and d) which confirmed the earlier reports.\textsuperscript{1,2} In addition, the tiny voltage drop at the beginning of discharge for all both electrodes indicating that the two r-GOP supercapacitors all have small internal charge transfer resistance and solution resistance.\textsuperscript{1-2,43}

![Figure 8](image)

Figure 8. (a) Specific capacitances obtained from GCD measurements as a function of current densities. (b) The capacitance retention of r-GOPs as a function of cycling number.

Furthermore, the specific capacitances were obtained from GCD measurements as the earlier reports.\textsuperscript{1} More importantly, the specific capacitances of the 0.7 and 1.2 μm thickness r-GOP were up to 235 and 174 F g\textsuperscript{-1} at 1 A g\textsuperscript{-1} (Figure 8a), respectively. They were much larger than that of other graphene paper electrodes which fabricated by other methods.\textsuperscript{2,39-41} And the capacitances all drop slowly with further increase of the discharge rate, and the high specific capacitances were still maintained even at the fast discharge rate of 10 A g\textsuperscript{-1}. These results indicate that the two different thickness r-GOP electrodes all have excellent rate
capability. The cyclic performance of the r-GOP electrodes were checked by the GCD cycling test at a current density of 1 A g\(^{-1}\) which is another key factor for supercapacitors. For the thicker electrode, about 86% of the initial capacitance was retained after 1000 cycles (Figure 8b), which indicate that it has excellent cycling stability. However, this is only about 70% of the thinner electrode. Such a case is most likely due to the poor mechanical performance of the thinner r-GOP films. It is easy to damage electrode in the process of assembling the supercapacitor.

3. CONCLUSIONS

In conclusion, we report an effective and simple method to prepare vertically aligned GOPs from GO suspensions by using an improved ESD\(_{\text{spr}}\) technique with a moving stage which is controlled by computer. After reduction by using HI acid, the r-GOPs with high integrity and good flexibility were successfully synthesized. The obtained r-GOP has an electrical conductivity as high as 6180 S/m, which is more than one and a half times of the r-GOP film which was fabricated by using the ESD\(_{\text{spr}}\) technique without moving stage. The experimental results approved for the first time that the arrangement and degree of alignment of r-GO sheets can affect the conductivity of the r-GOPs. Further electrochemical measurements for a symmetrical supercapacitor device based on the prepared r-GOP films indicate that it has great capacitive performance and electrochemical stability. It exhibited relatively high specific capacitance (174 F g\(^{-1}\)) at a current density of 1 A g\(^{-1}\) in 6 M KOH aqueous solution and its capacitance can retain approximately 86% after 1000 cycles. In addition, patterned freestanding r-GOPs which have potential applications in many fields such as stretchable electronics and wearable devices also can be fabricated by using this method.
4. EXPERIMENTAL SECTION

Fabrication of the GOPs

The ESD setup used in this work is schematically showed in Figure S1a. For fabricating the GOP films, the purchased single layer GO dispersion without any further treatment was fed into the needle by a syringe pump at a feeding rate of 30 μL min⁻¹, a voltage of 8 kV was applied between the needle and the polyamide nanofiber film/aluminum foil double-layer substrate (more details are included in Supporting Information) which was place on the two dimensional moving platform. The distance between the nozzle and substrate was set as 2.5 cm and a moving speed of the platform was set to 10 cm s⁻¹. The motion trail of X–Y axis is controlled by running the command program as shown in Figure S1b and the X-axis moving distance was set as 0.5 cm. After the deposition, the GOP films which achieve the expected thickness by adjusting the deposited times on the double-layer substrate were obtained as shown schematically in Figure S2a. In order to get free-standing GOPs, the polyamide nanofiber film of the double-layer substrate was dissolved by formic acid solution. So the GOP was separated from the aluminum foil. And then took out of the aluminum foil and sucked out the formic acid by using a dropper as shown schematically in Figure S2b-d.

Fabrication of the r-GOPs

As shown in Figure S2e and f, the reduction process was performed by immersing GOP into a HI acid solution and was heated at 100 °C for 1 h. And then the r-GOP film was washed with deionized water for several times. In the next step as shown schematically in Figure S2f-i, the r-GOP film was salvaged by a Teflon film to avoid the r-GOP film shrinking caused by the surface tension of the deionized water. Afterwards, the r-GOP on the Teflon film was put in draught drying cabinet at 60 °C for 4 h and then could
be readily peeled off from Teflon film because of the interfacial adhesion between them.

**Fabrication of the r-GOP**

For comparison, another reduced graphene oxide paper labeled r-GOP<sub>no</sub> was fabricated also by the aforementioned method and the only difference is keeping the collector substrate still in the ESD process.

**ASSOCIATED CONTENT**

**Supporting Information**

The detailed experimental materials and methods, the diagram of the electrospray/electrospinning system and schematic illustration of preparation procedures of r-GOP, and the Raman spectra of GOP and r-GOP.

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**Notes**

The authors declare no competing financial interest.

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