

**Electrochemically Exfoliated Graphene as Solution-
Processable, Highly-Conductive Electrodes for Organic
Electronics**

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Electrochemically Exfoliated Graphene as Solution- Processable, Highly-Conductive Electrodes for Organic Electronics

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ABSTRACT

Solution processable thin layer graphene is an intriguing nanomaterial with tremendous potential for electronic applications. In this work, we demonstrate that electrochemical exfoliation of graphite furnishes graphene sheets in high quality. The electrochemically exfoliated graphene (EG) contains a high yield (> 80 %) of 1 to 3 layer graphene flakes with high C/O ratio of 12.3 and low sheet resistance (4.8 k Ω /□ for a single EG sheet). Due to the solution-processability of EG, vacuum filtration method in association with dry transfer is introduced to produce large area and highly conductive graphene films on various substrates. Moreover, we demonstrate that the

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3 patterned EG can serve as high-performance source/drain (S/D) electrodes for organic field-
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5 effect transistor (OFETs).
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9 **KEYWORDS:** electrochemical exfoliation, high-quality graphene, solution-processing, organic
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11 field-effect transistors.
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16 A major challenge of organic electronics is the development of robust techniques for fabricating
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18 highly-conductive, flexible, and transparent electrodes.¹ The most widely used transparent
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20 electrode is indium tin oxide (ITO) which has an optical transparency of more than 80% in the
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22 visible light range, a favorable work function (~ 4.8 eV), and a low sheet resistance of 10 to 30
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24 Ω/\square .²⁻⁴ There are several limitations to ITO, however, such as sensitivity to acidic and basic
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26 environments, high surface roughness, and increasing cost due to the scarcity of indium. In
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28 addition, ITO is brittle which leads to microcracks when the material is bent as well as
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30 dramatically reduced conductivity. Many alternative materials have been developed to replace
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32 ITO such as conducting polymers like poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
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34 (PEDOT:PSS),⁵ carbon nanotubes (CNTs),^{6,7} metal grids, and metallic nanowires.^{8,9} Among
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36 these materials, CNT films exhibit high transparency across the visible light spectrum, but the
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38 high resistance at the junctions between carbon nanotubes obstructs conductive pathways within
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40 the film.¹⁰
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47 Graphene, which features high electrical conductivity, flexibility, and good mechanical and
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49 thermal stability, has emerged as a new-generation electrode material for organic electronic
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51 devices.¹¹⁻¹³ Graphene-based electrodes, obtained from either solution-processed reduced
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53 graphene oxide (rGO) or graphene grown by chemical vapor deposition (CVD) methods, have
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55 been used for organic photovoltaics,¹⁴ light-emitting diodes (OLEDs),¹⁵ field-effect transistors
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3 (OFETs), and^{16,17} photodetectors¹⁸. Electrodes prepared from rGO require chemical and/or
4 thermal treatment of GO to partially remove the oxygen-containing groups and to restore the
5 electrical properties. Chemical reduction by toxic hydrazine generally introduces impurities in
6 rGO¹⁹ while high-temperature treatment is incompatible with plastic or glass substrates.
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8 Moreover, high-quality graphene directly grown on Ni or Cu substrates by CVD requires a
9 multi-step transferring process involving the use of poly(methylmethacrylate) and/or
10 polydimethylsiloxane.^{20,21} The latter are difficult to remove and may even damage the graphene
11 film.^{22,23} Direct exfoliation of graphite in solution, such as electrochemical, sonochemical, and
12 liquid-phase exfoliation,²⁴⁻²⁸ allows for the fabrication of high-quality graphene electrodes *via* a
13 low temperature process. Nevertheless, the yields of graphene (typically 1 to 4 layers)
14 synthesized by these protocols remain low (< 50%). In addition, due to the poor solution-
15 processability of exfoliated graphenes in high-boiling point solvents (such as *N*-Methyl-2-
16 pyrrolidone (NMP) or *N,N'*-Dimethylformamide (DMF)), it is difficult to prepare graphene films
17 of a large area using conventional solution-processing techniques such as dip-coating,¹⁴ drop
18 casting,²⁸ spin coating,²⁹ spray casting,³⁰ ink-jet printing,³¹ and Langmuir-Blodgett deposition.³²
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20 Therefore, the development of a low-cost fabrication protocol leading to highly conductive,
21 uniform graphene films based on solution-processable graphene is highly desirable.
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44 In the present study, we demonstrate that electrochemical exfoliation of graphite furnishes
45 graphene sheets in high quality and high yield. The electrochemically exfoliated graphene (EG)
46 has a large sheet size (~ 10 μm), low oxygen content (*i.e.*, 7.5 at%), and low sheet resistance (4.8
47 $\text{k}\Omega/\square$) which are comparable to that of CVD graphene. Due to the solution-processability (~ 1
48 mg/mL in DMF) of such graphene sheets, large and homogeneous graphene films can be
49 fabricated on both rigid and flexible substrates by vacuum filtration and subsequent transfer to
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3 the desired substrates. The resulting graphene films exhibit sheet resistances of 4.1 and 2.4 k Ω/\square
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5 with transmittances of 85% and 73%, respectively. Patterned graphene films can serve as high-
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7 performance source/drain (S/D) electrodes for OFETs.
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10 11 **RESULTS AND DISCUSSION**

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14 The experimental setup for electrochemical exfoliation of graphite is illustrated in Figure 1a.
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16 Typically, natural graphite flakes, platinum wire, and 0.1 M H₂SO₄ solution were used as
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18 working electrodes, counter-electrodes, and electrolytes, respectively. When a positive voltage
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20 (*i.e.*, +10 V) was applied to a graphite electrode, the graphite flakes begin to expand, quickly
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22 dissociate, and spread into the solution (Figure 1b and c). The bias voltage was kept constant for
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24 2 min to complete the exfoliation process. Afterwards, the exfoliated graphitic materials was
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26 collected by vacuum filtration and washed repeatedly with water to remove the residual acid.
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28 Finally, the obtained powder was dispersed in DMF, resulting in EG sheets (Figure 1d). The
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30 yield of EG was generally higher than 60 % of the total amount of starting graphite materials.
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32 Notably, a dispersion of EG with a concentration up to 1.0 mg/mL in DMF can be obtained and
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34 remains stable for several weeks without evidence of agglomeration. Moreover, the exfoliation
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36 process can be readily scaled up. By using only ~ 2 cm long of graphite electrode, more than 350
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38 mg of EG was obtained in less than 5 min (Figure S1).
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46 The mechanism of graphite exfoliation in 0.1 M H₂SO₄ is depicted in Figure 1e: first, applying
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48 bias voltage results in the oxidation of water, producing hydroxyl (OH \cdot) and oxygen radicals
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50 (O \cdot).³³ Oxidation or hydroxylation by these radicals initially occurs at edge sites and grain
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52 boundaries of the graphite electrode. Second, defective sites at the edges or grain boundaries
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54 open up due to oxidation which facilitates intercalation by anionic SO₄²⁻. This process leads to
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3 the release of gaseous SO₂ and/or anion depolarization and causes expansion of the interlayer
4 distance of graphite.³⁴ To understand the role of electrolytes during the exfoliation process, we
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6 have performed control experiments using H₂SO₄ with higher concentrations (1.0 and 5.0 M).
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8 The exfoliation efficiency of graphite in 1.0 and 5.0 M H₂SO₄ was much lower than that in 0.1 M
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10 H₂SO₄, and the corresponding yield of EG was ~25% and ~7%, respectively. Exfoliation in 5.0
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12 M H₂SO₄ mainly generated fragments of graphite particle which rapidly suspends during
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14 exfoliation. Moreover, when a pure H₂SO₄ or H₂SO₄/acetic acid mixture (1:1 in ratio) was used
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16 as the electrolyte, the graphite electrode remained intact or slightly expanded due to the
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18 intercalation of negative ions when a voltage was applied for 2 h (Figure S2). These findings
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20 suggest that the presence of water in the electrolyte is crucial for the generation of oxygen or
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22 hydroxyl radicals that can react with graphite at the initial stage. When diluted H₂SO₄ (*i.e.* 0.05
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24 M and 0.01 M) was used, however, exfoliation only occurred at a higher voltage (+12.1 and
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26 +16.0 V for 0.05 M and 0.01 M, respectively) at a much lower rate (several hours were required).
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28 The EG yield for 0.05 M and 0.01 M H₂SO₄ was ~34% and ~2% respectively. The low
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30 exfoliation efficiency of EG in diluted H₂SO₄ is most likely due to the inefficient intercalation of
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32 anions into the graphite.
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36 The morphology and number of layers in the EG sheets were first investigated by atomic force
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38 microscopy (AFM) (Figure 2a). The EG sheet was deposited on SiO₂ using the Langmuir-
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40 Blodgett (LB) technique (Figure S3a). For a typical experiment, the EG dispersion in 1:3
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42 DMF/chloroform was added drop-wise onto the water surface. A faint black colored film was
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44 observed on the water surface after adding the EG dispersion. The film was compressed by LB
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46 trough barriers while the surface pressure was monitored using a tensiometer. Thus, EG sheets
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48 were uniformly deposited on SiO₂ by vertically dip-coating the substrate, followed by thermal
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annealing at 200 °C to remove the residual solvent. A histogram acquired across the boundary (inset of Figure 2a) revealed a mean thickness of ~0.86 nm (Figure 2a) for monolayer graphene which is 0.6 to 0.7 nm higher than that of pristine graphene on SiO₂.³⁵ This result implies that a certain amount of oxygen-containing groups decorates the graphene surface. The measured thickness of bilayer graphene was ~1.5 nm (Figure S3b). The thickness distribution of 80 samples of EG sheets calculated from the AFM height profile is shown in Figure 2b. Remarkably, more than 80 % of the graphene sheets comprised 1 to 3 layers with bilayer graphene (~ 35%) as a dominant product (Figure 2b). The size of the EG sheets was 5 to 10 μm which is much larger than the size of previously reported exfoliated graphene.^{24,25,27} Transmission electron microscopy (TEM) further confirmed a mean size of ~10 μm for EG (Figure S4). High-resolution TEM (HRTEM) studies provided further support that the EG sheets ranged from a single layer up to four layers (Figure 2c to e). A typical HRTEM image of bilayer graphene with an interlayer distance of ~0.34 nm is shown in Figure 2d. Moreover, the selected area electron diffraction (SAED) pattern (Figure 2f) of the graphene sheets exhibits the typical 6-fold symmetry, consistent with the hexagonal crystalline structure of a bilayer graphene sheet.³⁶

The chemical nature of the as-prepared EG sheets was investigated by X-ray photoelectron spectroscopy (XPS). Approximately 7.5 % of oxygen is present in EG, attributable to the oxidation of graphene which was unavoidable during the electrochemical process (Figure S5). Nevertheless, a high C/O ratio of about 12.3 can be achieved for EG, in contrast to rGO (C/O ratio ~3-10) obtained by chemical or thermal reduction of GO.^{37,38} The deconvoluted XPS spectra of the C 1s peak (~ 284 eV) further show the presence of 5.62 at% C-OH (285.4 eV) and 1.88 % C(O)-O (290.0 eV) functional groups (Figure 3a). The Raman spectra of a bilayer EG sheet displayed an intense 2D and G peak at ~2710 and ~1586 cm⁻¹, respectively (Figure 3b).

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3 Moreover, a defect-related D peak was observed at $\sim 1356\text{ cm}^{-1}$. The intensity ratio of D to G
4 (*i.e.*, I_D/I_G) was calculated to be 0.40. This is much lower than that of chemically or thermally
5 reduced GO (~ 1.2 to 1.5).^{39,40} The intensity ratio of 2D to G (*i.e.*, I_{2D}/I_G) is normally related to
6 the graphitization degree (for C=C sp^2 bonds) in graphitic carbons.⁴¹ The I_{2D}/I_G ratio (0.67) of
7 bilayer EG graphene sheets produced in this work is significantly higher than that of rGO^{42,43}
8 further suggesting the high quality of the EG.
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11 The electronic properties of the resulting EG sheets were examined by bottom-gate, top-contact
12 transistors based on a thin EG film or bilayer EG sheet. Thin-film and isolated sheets of EG on
13 $\text{SiO}_2/\text{p-Si}$ were prepared by the LB method. The thickness of the EG film ranged from 0.8 to 3.5
14 nm (roughness, R_a : 1.96 nm). The transfer curves of the devices are shown in Figure 4a and b.
15 Remarkably, the bilayer EG sheets exhibited a mean hole mobility of $\sim 233\text{ cm}^2/\text{Vs}$, which is
16 several times higher than that reported for electrochemically derived graphene ($5.5 - 17$
17 cm^2/Vs)²⁸ and reduced graphene oxide ($\sim 0.01 - 12\text{ cm}^2/\text{Vs}$).^{29,43-45} Moreover, the devices based
18 on EG thin-films delivered an average mobility of $34.6\text{ cm}^2/\text{Vs}$ with a maximum value of 47.3
19 cm^2/Vs (Figure 4b). The lower mobility of the EG thin-film compared to that of a single sheet
20 can be attributed to the inter-junction resistance between EG sheets. Further, the sheet resistance
21 R_s of a single EG sheet was measured by a two-point probe system. The calculated R_s was 4.8
22 $\text{k}\Omega/\square$, (Figure 4c) which was much lower than that of rGO and comparable to that of CVD
23 grown graphene.^{46,47} The work function of EG was examined by Kelvin probe force microscopy
24 (KPFM). A mean value of $4.90 \pm 0.05\text{ eV}$ (Figure 4d) was obtained which is slightly higher than
25 that of pristine graphene ($\sim 4.6\text{ eV}$).⁴⁸ The increased work function was due to the presence of
26 oxygen-containing functional groups that produced surface $\text{C}^{\delta+}-\text{O}^{\delta-}$ dipoles *via* the extraction of π
27 electrons from graphene.⁴⁹
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3 The high quality and solution-processability of the EG sheets led us to fabricate transparent
4 graphene films on different substrates using a vacuum filtration and dry transfer method. To this
5 end, an EG dispersion (~ 0.25 mg/mL) in DMF was first vacuum-filtered through a
6 polytetrafluoroethylene (PTFE) membrane. The filtered EG film was then pressed on a target
7 substrate such as glass or PET. When the PTFE membrane was peeled off, the EG film remained
8 on the target substrate due to van der Waals interactions between the graphene and substrate.
9 Unlike the vacuum filtration method in which the filter membrane must be dissolved in organic
10 solvents that may cause contamination,⁴⁵ the dry transfer method avoids dissolution of the filter
11 membrane which can then be reused for further experiments. Moreover, the thickness of the
12 transferred films can be adjusted through the filtration volume and the concentration of the
13 graphene dispersion. For example, vacuum filtration of 5 and 10 mL of EG dispersion yields
14 ~ 15 - and 25 -nm graphene films on substrates, respectively. The 15 - and 25 -nm thick graphene
15 films (diameter 50 mm) on PET had a transmittance of 85 % and 73 %, respectively (Figure 4e).
16 It can be seen from the optical microscopic (OM) images (Figure S6) that the transferred film
17 was uniformly covered on the substrates over large area. The average sheet resistance of the
18 transferred EG films measured using the four-point probe method (Figure 4f) was 16.0 and 8.2
19 $\text{k}\Omega/\square$ for 15 - and 25 -nm EG films. Remarkably, after thermal annealing of the EG films at 200
20 $^{\circ}\text{C}$ for 30 min, the sheet resistance dropped dramatically to 4.1 and 2.4 $\text{k}\Omega/\square$, respectively,
21 attributable to the evaporation of residual DMF. Further, a simple HNO_3 (65%) treatment of 15 -
22 and 25 - nm EG films significantly reduced the sheet resistance to 0.27 and 0.49 $\text{k}\Omega/\square$,
23 respectively (Figure S7).
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53 The simple graphene film transfer process provides a major advantage for the solution
54 fabrication of conductive electrodes for electronic devices. As a proof-of-concept, we
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3 demonstrated the fabrication of S/D electrodes for OFETs using patterned EG films. The
4 fabrication process for patterned graphene electrodes from EG films is illustrated in Figure 5a
5 (see Supporting information for experimental details). Briefly, an EG dispersion in DMF (~ 0.60
6 mg/mL) was vacuum-filtered through a PTFE membrane to obtain a 50-nm thick film and then
7 transferred to a SiO₂/p-Si substrate by a simple mechanical press (Figure S8a). Figure shows the
8 AFM image of uniformly transferred EG film on SiO₂/p-Si substrate. The conductivity of the
9 film was 590 S/cm which is higher than the previously reported 60-nm-thick rGO S/D electrodes
10 (500 S/cm) produced *via* thermal treatment.¹⁷ The patterned EG electrodes were obtained by
11 thermally evaporating aluminum (Al) on top of the EG film through a mask with subsequent
12 exposure to an O₂-plasma to remove the EG film from unmasked regions. Finally, Al was
13 chemically etched and EG-based S/D electrodes were generated (Figure 5b and S8b). A
14 conjugated donor-acceptor polymer, 4*H*-cyclopenta[1,2-*b*; 5,4-*b'*]dithiophene-
15 benzo[*c*][1,2,5]thiadiazole (CDT-BTZ-C16, Mw=10K Da, polydispersity index=2.67), was used
16 as the semiconductor due to its good solution-processability, close π -stacking distance, and
17 highly ordered lamellar packing structure on the surface.⁵⁰ The transfer and output characteristics
18 are shown in Figure 5e and f, respectively. Remarkably, a mean hole mobility of 0.50 cm²/Vs
19 (maximum mobility up to 0.60 cm²/Vs) with an on/off ratio exceeding 10⁶ was achieved. In
20 contrast, Au-based S/D electrodes produced a mean hole mobility of only 0.19 cm²/Vs
21 (maximum up to 0.21 cm²/Vs) with a lower on/off ratio (10⁵) (Figure S9a).⁵¹ For EG-based S/D
22 devices, the desirable linear and saturation regimes with apparent gate-voltage dependence
23 (Figure 5f) can be identified,^{52,53} in marked contrast to the S-shaped output curves derived from
24 Au-based devices (Figure S9b). This finding strongly suggests that graphene electrodes have a
25 low contact resistance with organic materials⁵⁴ which is the reason for the enhanced device
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3 performance. Furthermore, flexible OFETs based on EG S/D electrodes can be fabricated on a
4 PET substrate. In this case, the electrodes were first patterned on a filter (PTFE) membrane
5 followed by a dry transfer process on a PET substrate (Figure 6a). S/D electrodes (~50 nm thick)
6 were fabricated on the PTFE filter by protective metal (Al) followed by O₂-plasma etching
7 (Figure 6a). Afterwards, removal of the sacrificial Al layer in acidic solution afforded an EG film
8 patterned on the PTFE filter (Figure 6b). Finally, the EG electrodes were transferred to a PET
9 substrate by mechanically pressing the PTFE filter containing the patterns (Figure 6c). Thus, a
10 top-gate OFET device was constructed by using EG electrodes patterned on PET as S/D
11 electrodes (inset of Figure S10a). The transfer and output characteristics of flexible OFET are
12 shown in Figure S10 and a brief description is provided in Supporting Information. Although the
13 performance of flexible OFET is inferior to the device based on SiO₂/p-Si substrate, this study
14 shows the potential of high quality and solution-processable EG as electrode materials for
15 different electronic devices.
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33 34 35 **CONCLUSION**

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38 In conclusion, the present study demonstrates that electrochemical exfoliation of graphite is a
39 promising method for the fabrication of graphene sheets in high quality and high yield. The as-
40 prepared graphene has a large sheet size, low oxygen content and/or high C/O ratio as well as
41 excellent electronic properties comparable to CVD graphene. In addition, we introduce a vacuum
42 filtration method in association with the dry transfer method to produce highly conductive
43 graphene films on various substrates. The high solution-processability and high quality of the
44 exfoliated graphene sheets hold enormous promise for both rigid and flexible organic electronic
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16 *Supporting Information Available:* Experimental details, AFM, TEM images and XPS spectra of
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18 EG, photograph of electrochemical exfoliation in different electrolyte system, performance of Au
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20 electrodes and flexible EG based OFET devices. This material is available free of charge *via* the
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22 Internet at <http://pubs.acs.org>.
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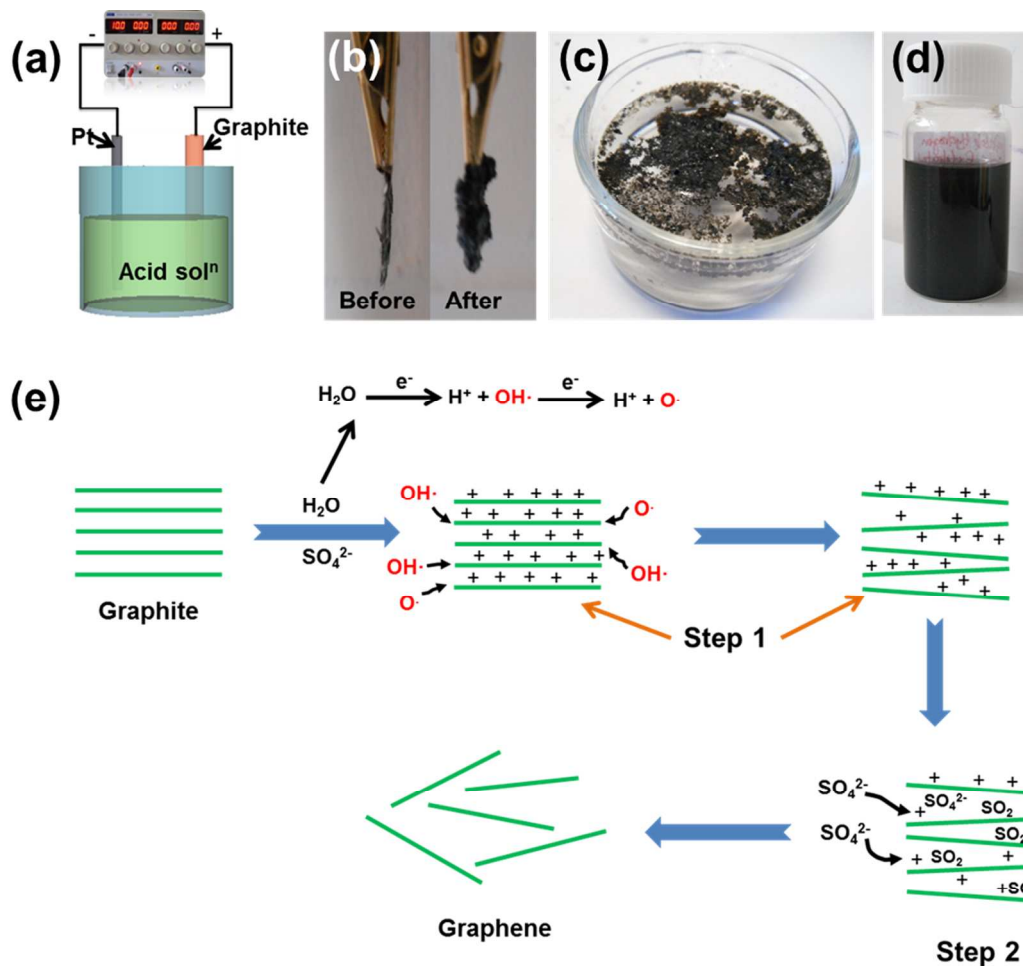


Figure 1: (a) Schematic illustration of the electrochemical exfoliation of graphite, (b) photographs of graphite flakes before and after exfoliation, (c) EG floating on top of water, (d) dispersed graphene sheets (~ 1 mg/mL) in DMF, and (e) schematic illustration of the proposed mechanism of electrochemical exfoliation.

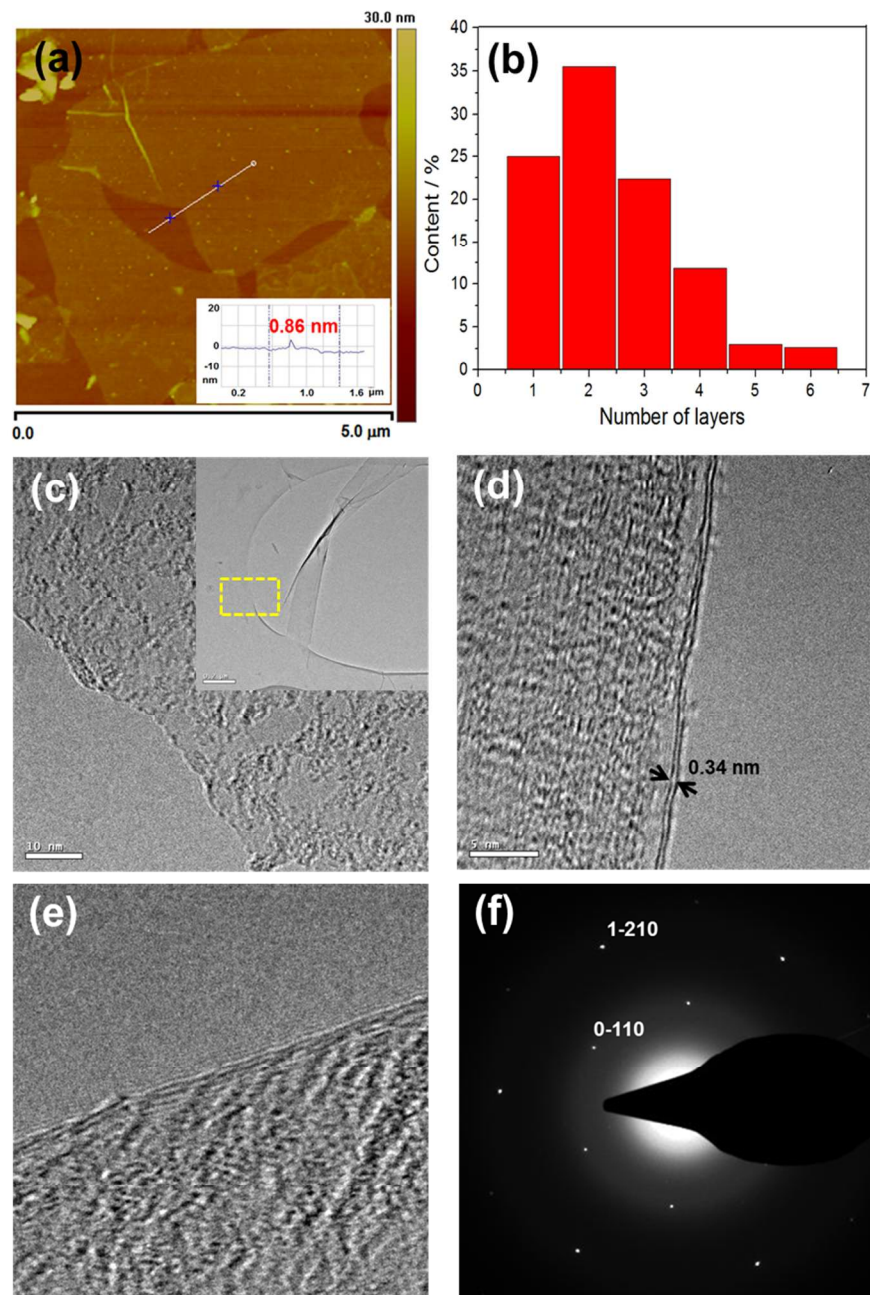


Figure 2: (a) Typical AFM image of the electrochemically exfoliated graphene on SiO₂, (b) statistical thickness analysis of the graphene sheets by AFM, (c), (d) and, (e) HRTEM images of single, bi and four layer graphene. The inset in (c) is the low magnification image of EG. To identify the number of graphene layers, the images are taken at the edge (as indicated by dashed box), (f) SAED pattern of a bilayer graphene.

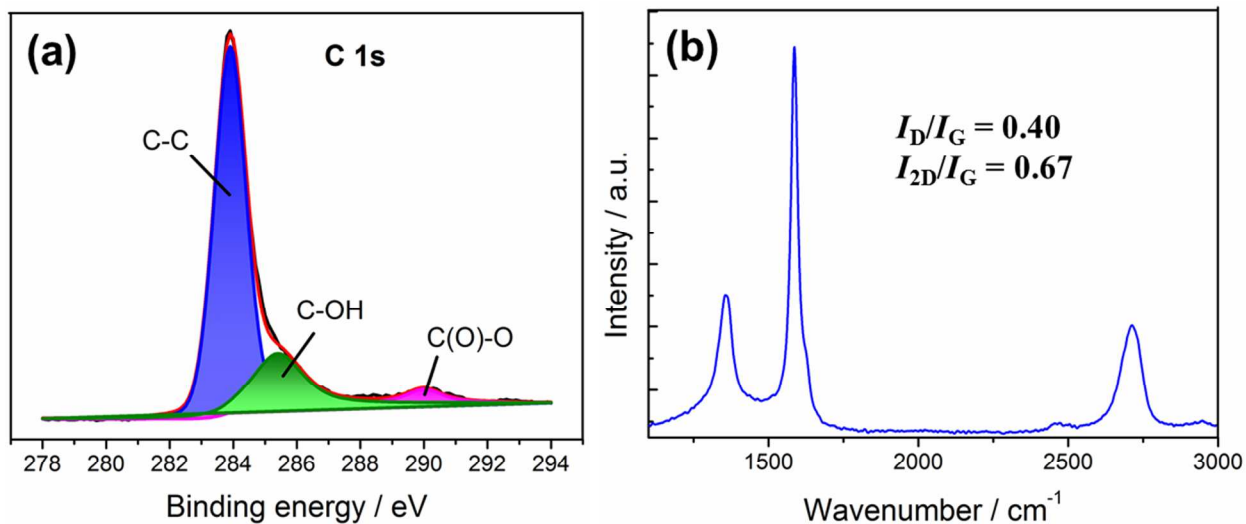


Figure 3: (a) High resolution XPS of C1s peak for EG and (b) Raman spectra (excited by 488 nm laser) of a selected bilayer EG sheet. The ratio of I_D/I_G and I_{2D}/I_G peaks are indicated in the figure.

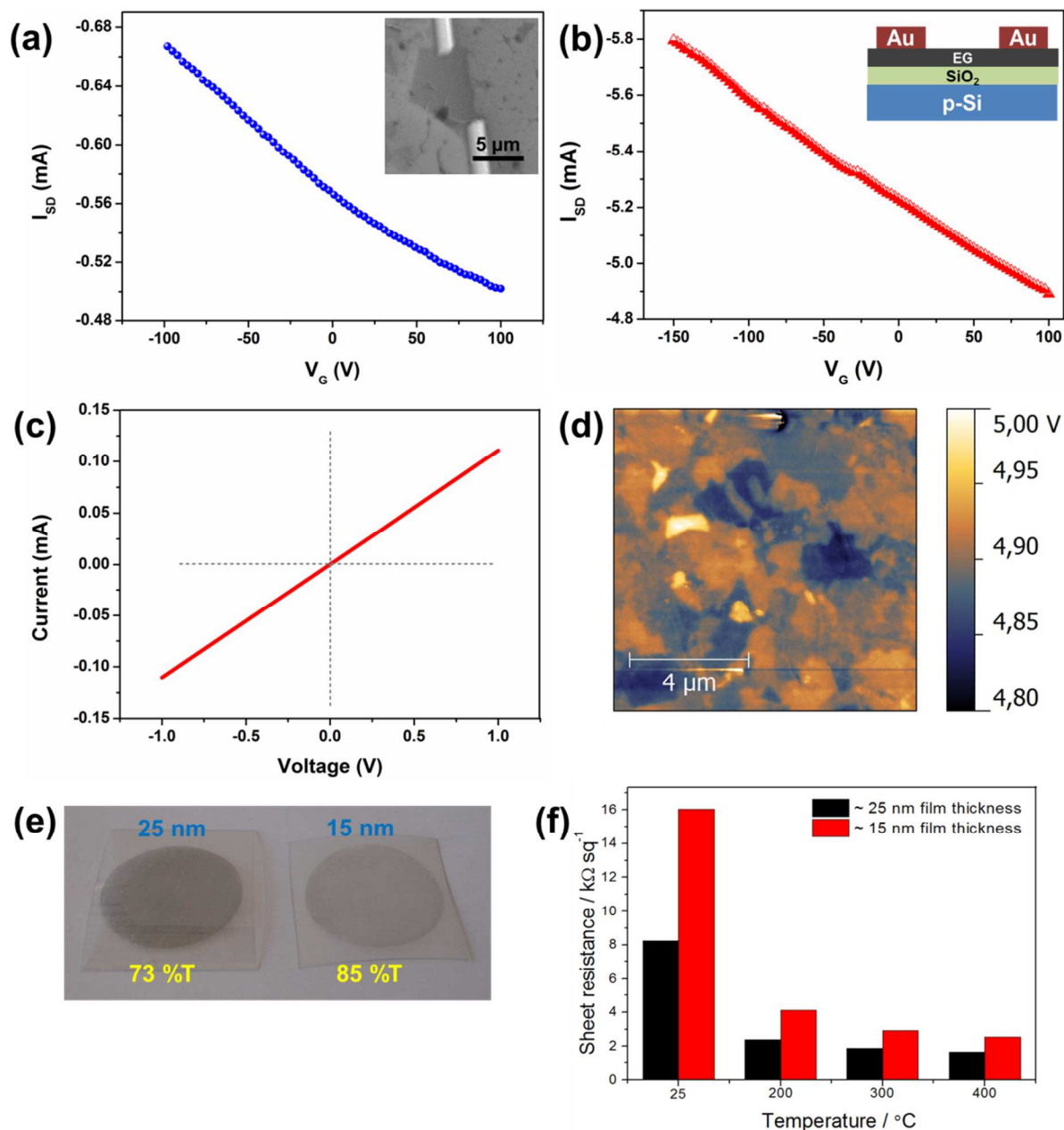


Figure 4: Transfer curve for a device prepared from (a) a bilayer EG sheet and (b) a thin EG film. Inset of (a) is an SEM image and that of (b) is the cross-section scheme of the fabricated device, (c) room-temperature I - V curve of a single bilayer EG sheet, (d) KPFM image showing the work function of EG, (e) photograph of the transferred graphene film on PET substrates and, (f) sheet resistance of EG films with different thicknesses.

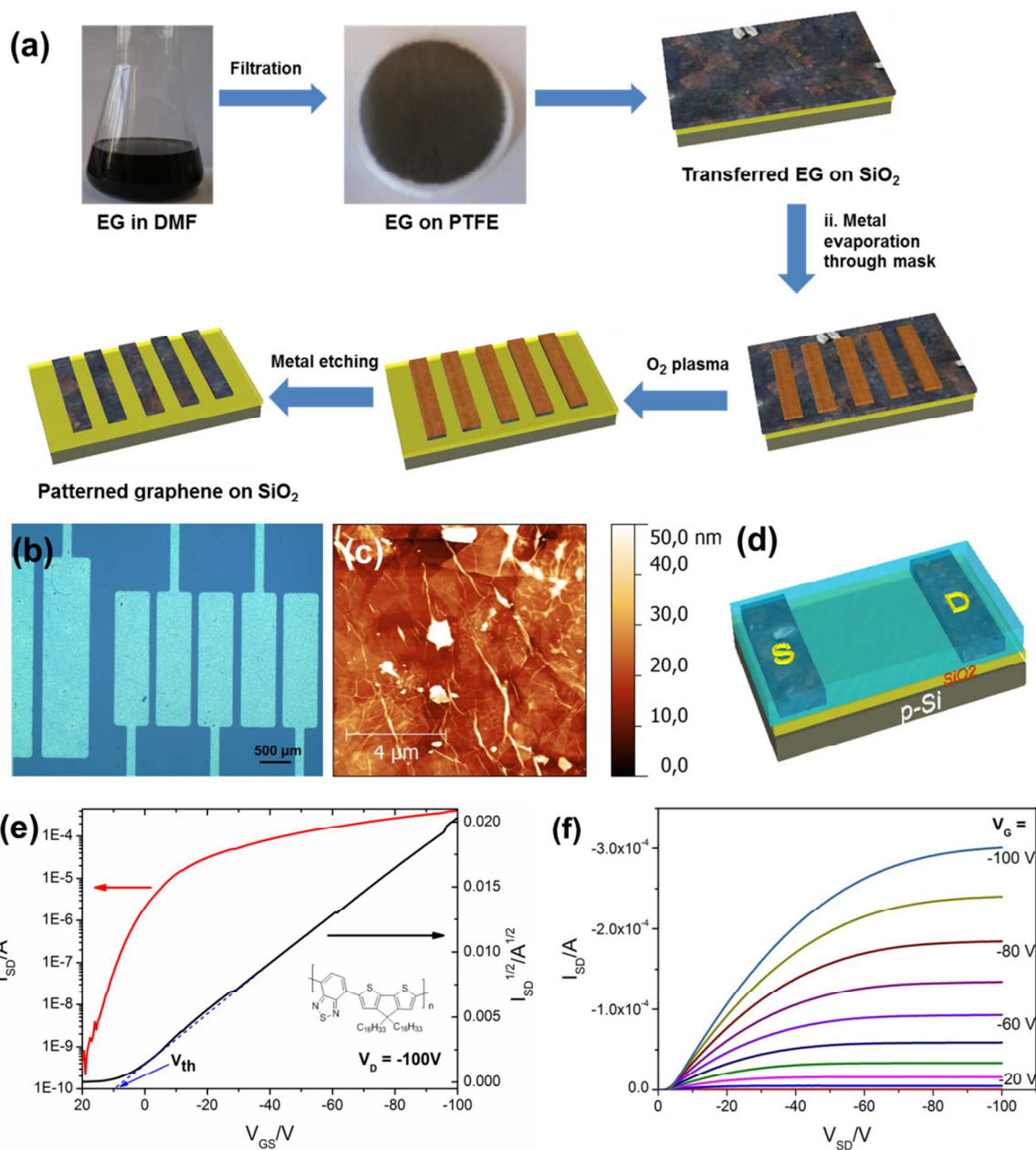


Figure 5: (a) Schematic illustration of the fabrication process of patterned EG S/D electrodes, (b) optical image of patterned EG S/D on a SiO₂/p-Si substrate, (c) typical AFM image of the 50-nm-thick EG electrode, (d) scheme of fabricated EG-based OFETs, (e) transfer characteristics of the CDT-BTZ-C16 based OFETs with EG S/D electrodes ($L/W = 1/18$) at a drain bias $V_D = -100$ V, and (f) output characteristics for various gate biases V_G . The molecular structure of CDT-BTZ-C16 is shown in the inset.

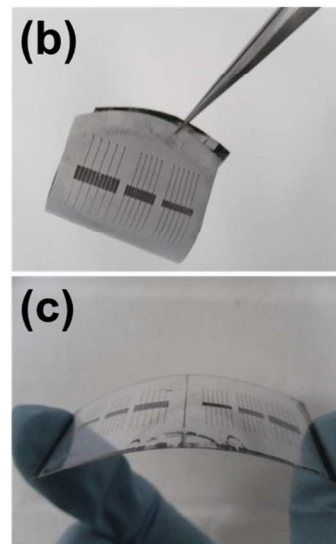
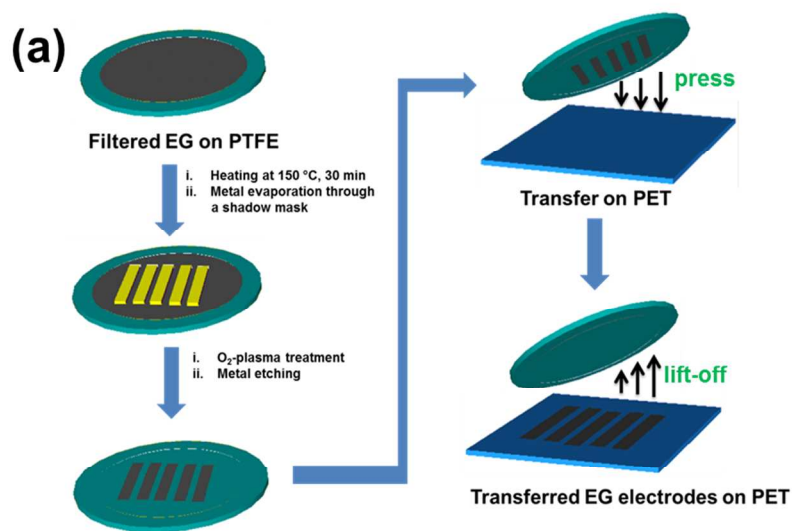


Figure 6: (a) Schematic illustration of the fabrication of patterned EG electrodes on PET substrates, (b) and photograph of EG electrodes patterned on PTFE membranes and (c) transferred on PET.

ToC Image

