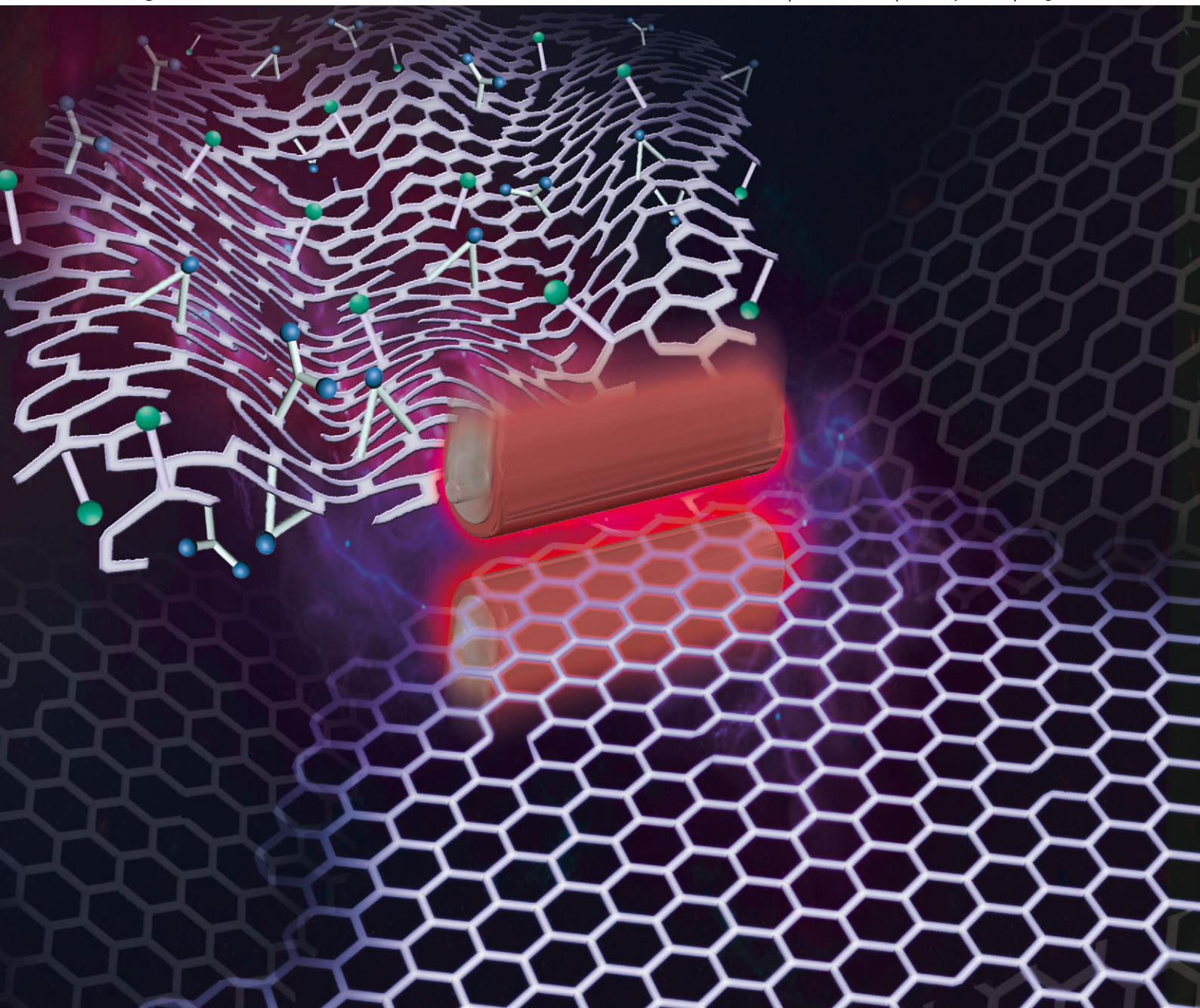


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Highly conductive reduced graphene oxide produced *via* pressure-assisted reduction at mild temperature for flexible and transparent electrodes†

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An effective approach to fabricate graphene-based conductive films is explored on the basis of the pressure-assisted reduction technique.

Solution-based synthesis of chemically exfoliated graphene oxide (GO) has received considerable attention compared to other approaches due to its low cost, scalability, and solution processability, and the GO-based conductive films with transparency and flexibility have been studied as transparent electrodes for potential applications as thin film transistors,^{1,2} sensors³ and organic photovoltaic devices.⁴

In general, the GO should be converted to reduced GO (rGO) to restore the high conductivity of graphene. Many publications have demonstrated the various reduction processes. Geng *et al.* reported a simple approach for preparing a transparent and conductive graphene film using controlled chemical reduction of exfoliated GO.⁵ Bao *et al.* reported that a post-annealing process at high temperature (>800 °C) was required to obtain rGO possessing good electrical properties.⁶ Although conventional thermal reduction processes have been reported to be more effective than chemical reduction processes, most of the previous methods were performed at high temperature with long reaction time, making it difficult to apply these processes to flexible substrates such as plastics. Moreover, these rGOs suffered from limitations such as high resistance and less uniformity of the surface, resulting in degraded electrical properties. Accordingly, an alternative reduction technique having the advantage of a fast, efficient, cost-effective, and mild temperature process applicable to

plastic substrates is still highly desired for rGO-based thin film applications.

Herein, we report a novel and reliable approach for the preparation of rGO transparent electrodes through the pressure-assisted reduction at relatively mild temperature. The electrical performance of the conductive film obtained by this process was enhanced due to the high restoration of GO as well as the dense packing of each graphene sheet. The densified rGO film formed a uniform surface with low surface resistance, allowing its practical application to gate electrodes of flexible organic thin film transistors (OTFTs). In a proof-of-concept demonstration, the rGO thin film-gated OTFT exhibited superior device performance in terms of mobility and the on/off ratio.

The rGO thin films were fabricated by three different reduction methods involving several stepwise procedures, as shown in Fig 1. First, the surface of the polyethersulfone (PES) film was modified by O₂ plasma treatment at ambient pressure to increase the wettability of the relatively hydrophobic substrate. In this study, GO thin films were readily deposited on the PES substrate with a good uniformity and coverage using a mixed solvent of ethanol and water. A previous

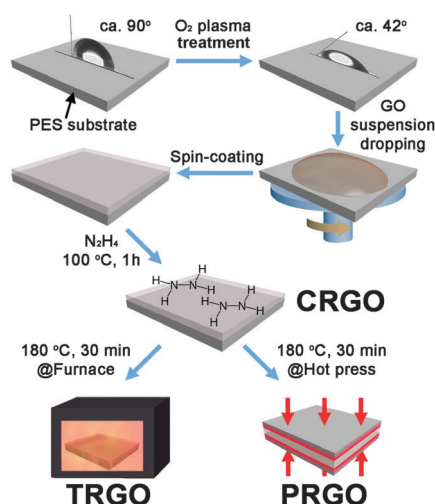


Fig. 1 Schematic illustration of PRGO thin film electrode fabrication by pressure-assisted thermal reduction.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, UV-Vis transmittance spectra of CRGO, TRGO, and PRGO films, XRD patterns of CRGO, TRGO, and PRGO, and optical image of the PRGO-gated OTFTs. See DOI: 10.1039/c3cc41874j

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study reported that the additive ethanol in the GO suspension can also control the surface chemistry and increase the uniformity and coverage of GO on the modified hydrophilic PES substrate.⁷ After spin-coating, electrically conductive rGO thin films were fabricated by reduction using chemical, chemical with thermal, and chemical with pressure-assisted thermal treatments. Hydrazine vapor at 100 °C was introduced to reduce the GO thin film, resulting in a chemically reduced graphene oxide (CRGO) thin film. Additional thermal reduction at relatively high temperature is required because chemical reduction alone is not sufficient to achieve the theoretical reduction limit. Therefore, subsequent reduction was carried out by loading the CRGO thin film in a furnace or hot press to enhance the reduction efficiency of thermally reduced graphene oxide (TRGO) or pressure-assisted reduced graphene oxide (PRGO) thin films at 180 °C, respectively.

A low sheet resistance is a prerequisite for rGO thin film applications to organic electrodes in electronic devices. Minimum sheet resistance values for CRGO, TRGO, and PRGO films were determined to be 190, 8.0, and 1.1 k Ω sq⁻¹, respectively. The sheet resistance was highly dependent on the degree of reduction, the presence of residual oxygen and nitrogen moieties, and the defects.⁸ For the PRGO film, sheet resistances decreased to $\sim 10^0$ k Ω sq⁻¹ with increasing pressure at about 78% of optical transparency (ESI[†]). Furthermore, the mechanical fatigue was investigated using a bending test machine to confirm the feasibility of using PRGO films as flexible organic electrodes (ESI[†]). The sheet resistance of PRGO thin films varied little up to 3000 bending cycles and recovered perfectly after unbending, making PRGO films potentially useful for flexible, transparent, and conductive electrodes.

To elucidate the origin of the decrease in sheet resistance, the surface morphologies of CRGO, TRGO, and PRGO thin films were further investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface of the PRGO thin film was dramatically flattened compared to those of CRGO and TRGO thin films. The wrinkles shown in Fig. 2a are characteristic of CRGO, corresponding to the images published in the literature.⁹ In general, graphene has a negative thermal expansion coefficient and its unique property causes the formation of wrinkles.¹⁰ This intrinsic feature can be significantly suppressed when the graphene sheets are strongly bonded to a substrate such as mica.¹¹ In this work, there is very little formation of wrinkles on the PRGO thin film because the thermal expansion coefficient of PRGO shifted to the positive direction.¹² Particularly, PES as a plastic substrate has sufficient interaction with the PRGO sheets, reducing the number of wrinkles.¹³ The pressure applied to the PRGO thin film also enhances the interaction between the film and the substrate.¹⁴

Furthermore, the wrinkles cause surface roughness that acts as a defect leading to higher sheet resistance. Not only the high sheet resistance of the CRGO film, but also its rough surface can potentially limit the integration of CRGO films into organic electronics because the roughness of the bottom layer of a device often governs the interface and morphology of the upper layer, which may result in highly tortuous current flow.¹⁵ In contrast, the TRGO and PRGO thin films had fewer wrinkles compared to the CRGO film as shown in Fig. 2b and c.

Based on AFM measurements (Fig. 2d–f), the RMS roughness values of CRGO, TRGO, and PRGO thin films were 10.1, 4.78, and

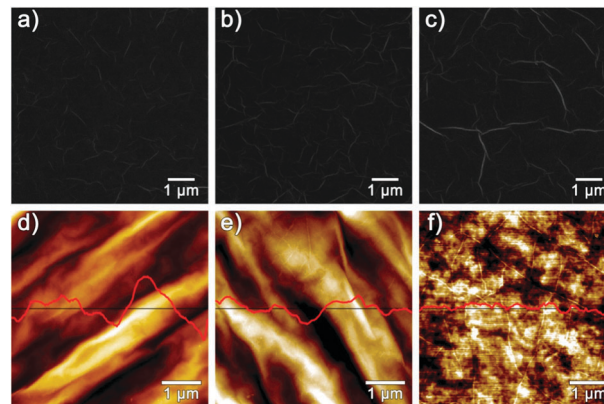


Fig. 2 (a–c) SEM images and (d–f) AFM images of CRGO, TRGO, and PRGO films, respectively.

1.61 nm, respectively. The decrease in surface roughness indicated that the pressure-assisted reduction process provided a much smoother PRGO thin film compared to conventional chemical and/or thermal reduction processes. The low surface roughness is closely related to low sheet resistance. Thus, the PRGO thin film with a flat surface topography exhibited superior electrical properties.

X-ray photoelectron spectroscopy (XPS) analysis was performed to determine the content and configuration of carbon, oxygen, and nitrogen in rGO films prepared by different reduction methods (ESI[†]). The conventional CRGO showed the characteristic C–C peak at 284.5 eV, as well as four additional peaks that were deconvoluted, indicating the presence of functional groups; C–N at 285.5 eV, C–O at 285.5 eV, C=O at 287.5 eV, and O–C=O at 289.4 eV. Less oxygen and nitrogen were observed in PRGO compared to CRGO and TRGO in Fig. S1 (ESI[†]). Furthermore, the C/O atomic ratio was analyzed to evaluate the degree of reduction of GO. The C/O atomic ratios of GO, CRGO, TRGO and PRGO were 3.0, 6.9, 8.6, and 10, respectively (Table S1, ESI[†]). The high C/O ratio of PRGO resulted from the high degree of reduction, providing higher electrical conductivity compared to CRGO and TRGO. These results correspond to the low sheet resistance of PRGO. In addition, X-ray diffraction (XRD) analysis results manifest that the PRGO thin film has a smaller interlayer spacing value than the others (ESI[†]). Thus, the pressure-assisted reduction process is an alternative method for removing functional groups and impurities at a relatively mild temperature.

The novel reduction process used in this study resulted in PRGO thin films with low sheet resistance and low surface roughness due to higher restoration of the conjugated π -orbital system and smaller interlayer spacing compared to CRGO and TRGO thin films. In this point of view, understanding the mechanism by which the pressure-assisted reduction process reduces GO is important. Fig. 3 demonstrates a schematic diagram comparing the heat flow between TRGO and PRGO processes. The heat flow *via* different reduction processes was correlated with reduction efficiency based on the contact area at the interface between the heat source and the PES substrate. In the case of thermal reduction for TRGO, the surfaces of the two bodies, consisting of the upper side of the heat source and the bottom face of the PES film, were not uniform, leading to the formation of voids. Heat transfer by the thermal reduction

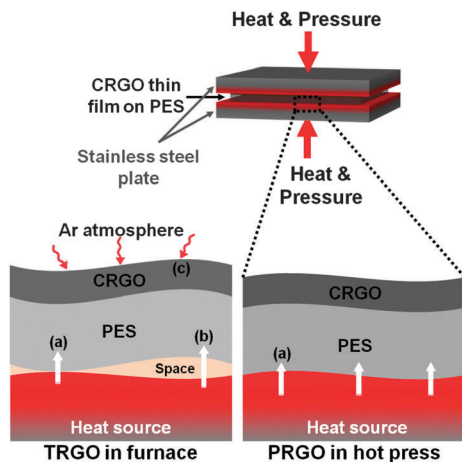


Fig. 3 Schematic illustration of heat transfer from the heat source to CRGO thin films via (a) direct contact, (b) electromagnetic field and/or heat diffusion, and (c) convection and radiation.

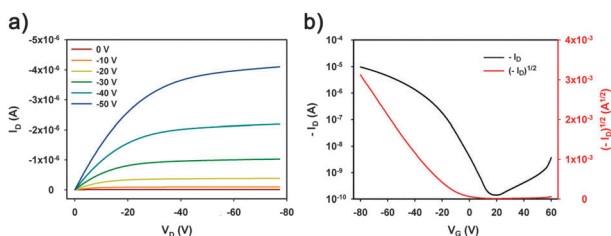


Fig. 4 Electrical output and transfer characteristics of pentacene OTFTs with PRGO gate electrodes.

process can occur in voids as well as between two solid bodies *via* heat diffusion, and direct contact. In the case of pressure-assisted reduction for PRGO, however, pressure can squeeze the two bodies between the CRGO film and the substrate, minimizing the number of voids and maximizing the area of direct contact. Heat flow by direct contact in a hot press is 100 times higher than that by indirect and convective heat transfer in a furnace at the same reduction temperature.¹⁶ Furthermore, the upper body of the hot press confines the thermal energy inside GO layers, thereby enhancing the heat transfer from the heat source to GO. As a result, pressure-assisted reduction transfers sufficient energy to dissociate functional groups from GO thin films, increasing the reduction efficiency and the C/O ratio. This hypothesis is consistent with our experimental data. Therefore, the proposed process offers an alternative route for the reduction of GO from a GO suspension, allowing device fabrication on any plastic substrate.

Pressure-assisted reduction enabled the simple fabrication of a high-performance OTFT with a flexible, transparent, and flat PRGO thin-film electrode having superior electrical properties. Bottom-gate OTFTs were prepared using thermally evaporated gold and pentacene as a source-drain (S-D) electrode and semiconductor, respectively (ESI[†]). Fig. 4 presents (a) drain current–drain voltage (I_D – V_D) and (b) drain current–gate voltage (I_D – V_G) characteristics of fabricated OTFTs. Under the experimental conditions, a

field-effect mobility of $0.18 \pm 0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, a threshold voltage of -18.18 V , and an on/off current ratio of 6.94×10^4 were obtained. The PRGO electrodes showed superior electrical performance due to reduced contact resistance resulting from the smooth surface of the graphene electrode.¹⁷

In conclusion, a reliable and effective method was proposed for fabricating graphene-based conductive films using pressure-assisted reduction. The as-prepared graphene-based thin films exhibited superior optoelectronic properties and mechanical flexibility. SEM and AFM analysis showed few wrinkles on the PRGO surface, leading to superior electrical properties. XPS spectra confirmed the removal of oxygen- and nitrogen-containing functional groups, corresponding to the small interlayer spacing of PRGO. The origin of these PRGO properties was attributed to the increased heat flow caused by greater direct contact between the heat source and the plastic substrate. The proposed reduction process offers an alternative route for incorporating the fundamental properties of rGO into technologically viable devices. Furthermore, PRGO thin films were applied to the gate electrode of a flexible OTFT, exhibiting superior performance compared with the conventional gold electrode. This approach is versatile and scalable, and is adaptable to a wide variety of applications.

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