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Plasma-Assisted Reduction of Graphene Oxide at Low Temperature and Atmospheric Pressure for Flexible Conductor Applications

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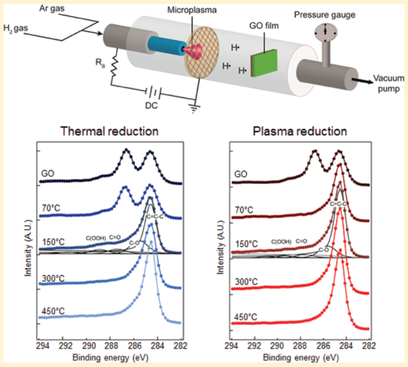
Ⓢ *Supporting Information*

ABSTRACT: Reduction of graphene oxide (GO) at low temperature and atmospheric pressure via plasma-assisted chemistry is demonstrated. Hydrogen gas is continuously dissociated in a microplasma to generate atomic hydrogen, which flows from the remote plasma to thin films of GO deposited on a substrate. Direct interaction with ions and other energetic species is avoided to mitigate ion-induced sputter removal or damage. The residual oxygen content and structure of the GO films after plasma treatment is systematically characterized at different temperatures and correlated to the conductivity of the films. For example, at 150 °C, we find that the plasma-reduced GO contains less than 12.5% oxygen and exhibits a sheet resistance of 4.77 × 10^4 Ω/sq, as compared with thermal reduction alone, which results in 22.9% oxygen and a sheet resistance of 2.14 × 10^6 Ω/sq. Overall, the effective removal of oxygen functional groups by atomic hydrogen enables large-scale applications of GO as flexible conductors to be realized.



SECTION: Nanoparticles and Nanostructures

Graphene, because of its unique structure and properties,[1,2] has elicited enormous interest for field effect transistors (FETs),[3] transparent conductive films,[4,5] lithium-ion batteries,[6] supercapacitors,[7] organic photovoltaic cells,[8,9] electron field emitters,[10] ultrasensitive sensors,[11] and hydrogen storage.[12−14] So far, several methods have been developed to produce graphene including mechanical cleavage of highly oriented pyrolytic graphite (HOPG),[15] sublimation of silicon from silicon carbide,[16,17] and thermal[18,19] or plasma-enhanced[20] chemical vapor deposition (CVD) from a carbon feedstock gas. Graphene oxide (GO) is a promising alternative for bulk production of graphene-based materials as it can be synthesized in large quantities from inexpensive graphite powder[21] and solubilized in a variety of solvents.[22] The preparation of a dispersed form of graphene is attractive for low-cost, solution-phase processing of flexible electronic devices.[22]

A critical challenge for technological applications of GO is the presence of oxygen functional groups that must be controlled to precisely tune their electronic and optical properties.[23] GO is typically reduced in solution by strong chemical reducing agents such as hydrazine (N_2H_4)[24,25] or sodium borohydride ($NaBH_4$).[26] However, the treatment of GO with these chemicals is time-consuming and generally ineffective, often requiring additional annealing steps.[5,27] Additionally, hydrazine (in the form of hydrate[28]or dimethylhydrazine vapor[29]) is a dangerous and environmentally toxic chemical that can introduce impurities in the reduced GO. Alternatively, thermal annealing in Ar, H_2, or ultrahigh vacuum (UHV) environments has been found to remove oxygen effectively,[23,30] but the high temperatures that are required limit the range of substrates that can be used. For this reason, novel low-temperature, green approaches to GO reduction have been introduced such as flash reduction[31] and electrochemical reduction.[32]

Compared with other chemical techniques, plasma discharges offer a unique advantage because nonequilibrium reactions can be performed at low temperature and high purity.[33] In the case of GO, the generation of atomic hydrogen could enable effective removal of oxygen functional groups.[27] However, plasmas contain energetic species such as ions that can bombard and sputter or damage such atomically thin materials.[34] Here we report on a remote, high-pressure plasma process for GO reduction that completely eliminates the direct interaction of ions and electrons with the GO film while also permitting atmospheric-pressure treatment. Hydrogen gas is continuously dissociated in a microplasma to produce atomic hydrogen and carried by the gas flow to react with and remove oxygen functional groups from GO films at low temperatures (<150 °C) via radical-assisted chemistry. We show that the residual oxygen content in the GO films after plasma-assisted reduction is lower than thermal reduction alone at the same temperature and comparable to results for thermal reduction at higher temperatures. This allows GO to be directly reduced on polymeric substrates such as poly(ethylene terephthalate)

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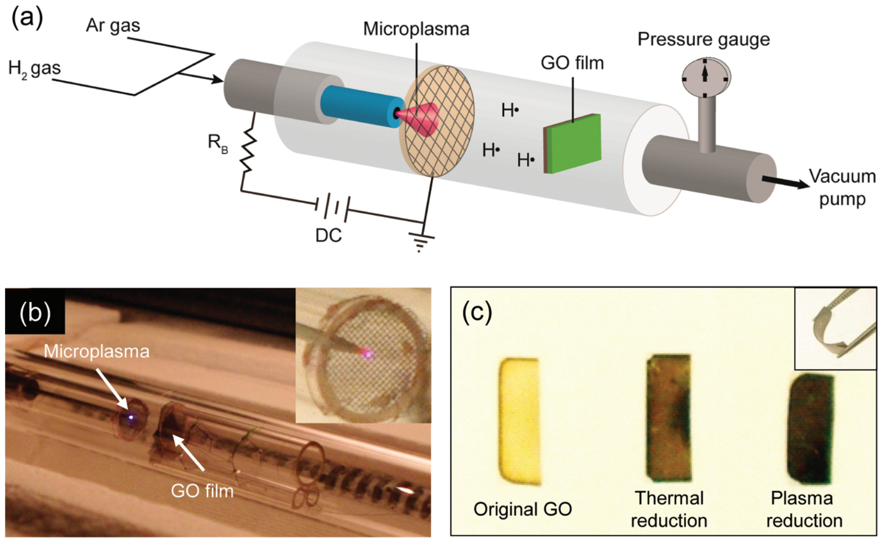

Figure 1. (a) Schematic diagram of experimental setup used for remote, atmospheric-pressure plasma-assisted reduction of GO thin films. A DC microplasma housed inside a quartz tube is formed between a negatively biased stainless-steel capillary tube and a grounded stainless-steel mesh electrode. Gas mixtures of Ar and H_2 are introduced into the microplasma to generate atomic hydrogen (H●). Thin films of GO were drop cast on substrates and placed 1.5 cm from the microplasma to avoid ion and electron bombardment. (b) Photograph of remote microplasma, operated in Ar/H_2 (50/50) at a discharge current of 10 mA and GO film (inset: close-up of microplasma). (c) Photographs of GO films deposited on PET substrates before reduction (left panel) and after thermal treatment at 150 °C (middle panel) or plasma treatment at 150 °C (right panel). All treatments were performed in an Ar/H_2 atmosphere (50/50) at 1 atm (inset: flexibility of GO films after plasma-assisted reduction is demonstrated).

(PET) to obtain highly conductive films. The unique combination of low temperature, atmospheric pressure, and high purity suggests that this nonequilibrium chemical approach can be used for roll-to-roll processing of GO films for large-scale, flexible conductor applications.

Figure 1a schematically illustrates the experimental setup that was used to reduce films of GO consisting of a remote, atmospheric-pressure microplasma and a tube furnace (Thermolyne 79300). Gas flow was coupled to the microplasma by high-pressure gas fittings; all flow rates were controlled by digital mass flow controllers. The microplasma was operated with a DC power supply (Keithley, model 246) between a negatively biased stainless-steel capillary tube (I.D. = 180 μm, L = 5 cm, Restek) and a grounded stainless-steel mesh (Figure 1b), separated by 2 mm. To ignite the plasma, we applied a high voltage (~2 kV). After gas breakdown, the discharge current was controlled by an inline resistor (160 kΩ) on the high voltage side. Excited species generated in the plasma including atomic hydrogen were detected by optical emission spectroscopy (OES, Ocean Optics HR 4000). The light was collected from the plasma with a fiber optic cable. Spectra were integrated 10 times with an exposure time of 300 ms per scan to obtain a high signal-to-noise.

GO was synthesized from graphite flakes (Asbury Carbons) by a modified Hummers method.[35] GO films were prepared by drop casting the aqueous suspension on Au foil (25 μm, ESPI) or Au-coated Si (300 nm, Sigma Aldrich) for chemical analysis, or PET for sheet resistance measurements. Before each experiment, the GO film was loaded into the quartz tube reactor and placed 1.5 cm downstream from the grounded stainless-steel mesh in the afterglow, where charged species in the plasma cannot interact with the film.[36] The reactor was then repeatedly evacuated by an oil-free, dry pump (Welch Vacuum, model 2562B-01) and purged to remove air and water before being brought up to atmospheric pressure with the desired gas flow; atmospheric pressure was maintained during the experiments by exhausting the gas from the reactor without active pumping. The GO films were then treated for 30 min by heating alone or with heating and the plasma operating at a constant discharge current. At the end of each experiment, the plasma and/or heating were shut off, and the furnace was cooled with a gas flow of Ar. Figure 1c shows representative photos of GO films on PET before treatment (left panel) and after either thermal annealing (middle panel) or plasma exposure (right panel). It is readily apparent that the plasma treatment results in a darker film. The inset of Figure 1c confirms that the GO films reduced on PET remain flexible after plasma treatment.

The present study focuses on understanding the effectiveness of GO reduction by atomic hydrogen. To decouple the role of atomic hydrogen, we systematically studied the reduction of GO by the following methods of treatment (i) thermal annealing alone (in an Ar/H_2 atmosphere), (ii) remote Ar plasma with thermal annealing, and (iii) remote Ar/H_2 plasma with thermal annealing. All treatments were performed at atmospheric pressure, and we focused on low temperatures, which are suitable for flexible conductor applications. We note that even without any heating by the furnace, the plasma itself was found to raise the temperature of the substrate through convective heat transfer. The temperature was found to depend on several process parameters including discharge current, gas composition, and distance from the discharge. For the specifications used in this study, we measured a temperature of ~70 °C; this was then assumed to be the minimum temperature for our study. (See the Supporting Information.) We believe that lower temperatures could be accessed by our process by increasing the distance of the substrate from the discharge or lowering the discharge current.

To confirm the generation of atomic hydrogen in the plasma, we employed OES. OES is a powerful tool for characterization of excited states present in a plasma environment and is particularly useful for microplasmas because it is noninvasive. Figure 2a,b shows spectra obtained from a microplasma formed

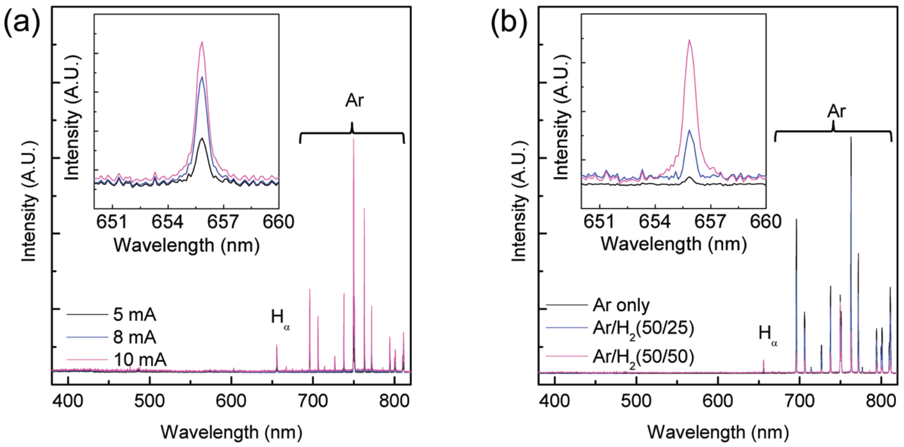

Figure 2. Optical emission spectra of Ar/H_2 microplasma as a function of (a) discharge current and (b) H_2 composition. Lines corresponding to Ar excited states and atomic hydrogen (H_α) are indicated.

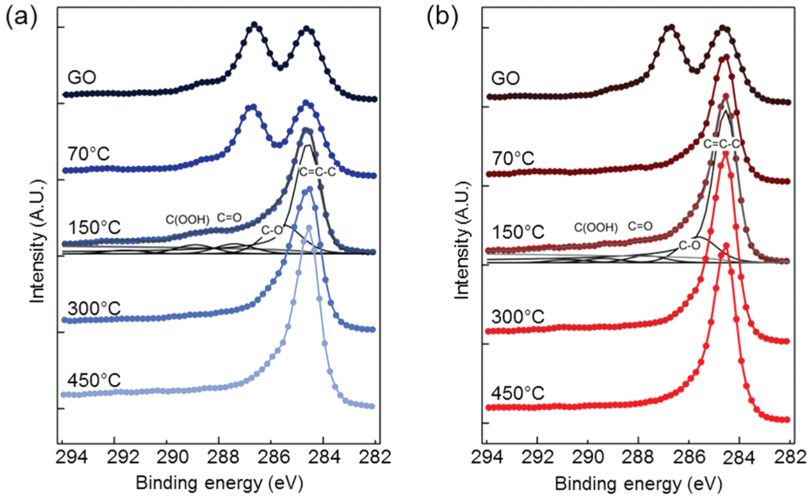

Figure 3. (a) C 1s high-resolution XPS spectra of GO thin films before and after thermal reduction in an Ar/H_2 (50/50) background. (b) C 1s high-resolution XPS spectra of GO thin films before and after Ar/H_2 (50/50) plasma-assisted reduction at various temperatures (discharge current = 10 mA). All reduction was performed at atmospheric pressure for 30 min. The spectra were fit by Doniach–Sunjic function after subtracting a Shirley background, as indicated for the spectra at 150 °C. The different components related to various chemical shifts of carbon bonds are indicated.

in a gas mixture of Ar/H_2 at various discharge currents. Overall, intense lines corresponding to Ar are observed in the range of 700 to 800 nm. Importantly, we find a peak at 656.3 nm, which corresponds to atomic hydrogen (H_α). Of the three possible states of atomic hydrogen known as the Balmer series, the H_α peak is the most abundant species and easiest to observe by OES.[37,38] The relative intensity of the H_α peak is found to increase with discharge current in accordance with an increase in the plasma density.[30] Increasing the H_2 flow rate (relative to Ar) also increases the intensity of this peak.

The oxygen bonding in the GO films after the various forms of treatment was evaluated by X-ray photoelectron spectroscopy (XPS), which was carried out with a PHI VersaProbe spectrometer (Al Kα). Figure 3a,b shows the carbon 1s (C 1s) core-level spectra collected from GO films after thermal annealing and remote atmospheric-pressure microplasma exposure at various temperatures – both types of treatment were performed in identical Ar/H_2 atmospheres. The C 1s signal of the initial fully oxidized GO film is also shown and consists of different components that can be deconvoluted into C=C/C–C (284.6 eV), C–O (286.1 eV), C=O (287.5 eV), C(=O)•(OH) (289.2 eV), and π–π* satellite peak (290.6 eV). These assignments are consistent with previous reports of GO.[23] After remote plasma exposure at 70 °C, the peaks corresponding to C–O (286.1 eV), C=O (287.5 eV), and C(=O)•(OH) (289.2 eV) were reduced. (See Figure 3b.) In comparison, thermal annealing at 70 °C did not show any significant change to the structure of the C 1s band of GO. At 150 °C, both thermal and plasma-assisted reduction resulted in a decrease in the intensity of peaks corresponding to oxygen species, but the latter produced a more significant change, particularly in regards to C=O and C(=O)•(OH). With increasing temperature, the oxygen species are present in lesser amounts for both types of treatment, consistent with prior reports for thermal annealing of GO.[23]

The atomic percentages of the various carbon bonds in the reduced GO films were determined by analyzing the C 1s XPS spectra at 150 °C (Table 1). The majority of oxygen species in the pristine GO film are in the form of C–O bonds. Plasma-assisted reduction was found to more effectively reduce the number of C–O bonds as well as C=O and C(=O)•(OH) species that have been found to decorate the edges of GO sheets and are believed to be more difficult to remove.[39]

The overall oxygen content in the treated GO films was obtained as a function of temperature from XPS survey spectra.

Table 1. Atomic Percentages of Different Carbon Bonds Identified by XPS in GO Thin Films Reduced by Thermal Treatment Only and Plasma-Assisted Treatment in an Ar/H_2 Atmosphere at 150 °C and 1 atm

	C=C/C−C	C−O	C=O	C(=O) •(OH)
thermal reduction	72	16	6.4	5.6
plasma-assisted reduction	83.4	12.7	2.1	1.8

(See the Supporting Information.) The ratio of carbon to oxygen was estimated by dividing the area of the C ls and O1s peaks and multiplying by the photoionization cross sections. Figure 4a,b shows the atomic percentage (C 1s %, O1s %) and atomic ratio (C 1s/O 1s), respectively, after each treatment, and the calculated results are summarized in Table 2. The C/O atomic ratio is found to be significantly higher for plasma-reduced GO (6.95) than thermally reduced GO (3.37) at 150 °C; in fact, this value is even higher than GO thermally reduced at 300 °C (6.35). Whereas the oxygen content in the GO films after thermal reduction (22.9%) and Ar plasma-assisted reduction (21.2%) are similar and relatively high, the addition of H_2 to the plasma (12.5%) results in a significant removal of oxygen functional groups. This confirms that atomic hydrogen leads to enhanced reduction of GO at low process temperatures. Moreover, the similar levels of oxygen in GO films after thermal reduction and Ar plasma-assisted reduction confirms that there is no significant ion bombardment in our remote plasma system because low-energy ions are sufficient to remove oxygen.[40]

Structural changes to the GO films as a result of plasma exposure were evaluated by micro Raman spectroscopy. Raman spectra were collected with a Jobin-Yvon Horiba LabRam system at an excitation wavelength of 633 nm and 17 mW power, which was low enough to avoid damage to the samples during measurements. (See the Supporting Information.) Figure 5 shows a series of Raman spectra obtained for GO films treated by thermal reduction alone, Ar plasma-assisted reduction, and Ar/H_2 plasma-assisted reduction. The Raman spectrum of the as-deposited GO film reveals a D-band at 1350 cm^{-1} and a G-band at 1600 cm^{-1}, the latter corresponding to the first-order scattering of the E2g mode.[41,42] The prominent D peak is due to structural imperfections created by oxygen functional groups in the carbon basal plane. After each of the various treatments, no significant changes were observed in the spectra. According to Tuinstra and Koenig,[43] the in-plane sp^2 crystallize size can be estimated from the ratio of the intensity of the D to G peaks (I_D/I_G).

Table 2. XPS Analysis of Carbon and Oxygen Content and C 1s/O 1s (Atomic Ratios) and Sheet Resistance in As-Prepared GO Thin Films and Reduced GO Thin Films after Various Methods of Treatment[a]

	C (%)	O (%)	C/O	sheet resistance (Ω/sq)
GO	66.09	33.91	1.95	∞
thermal reduction (150 °C)	77.10	22.90	3.37	2.14×10^6
Ar plasma-assisted reduction (150 °C)	78.80	21.20	3.72	
Ar/H_2 plasma-assisted (150 °C)	87.50	12.50	6.95	4.77×10^4
thermal reduction (300 °C)	86.40	13.60	6.35	

[a] Temperature was 150 °C and the pressure was 1 atm for all treatments. Thermal treatments were performed in an Ar/H_2 atmosphere.

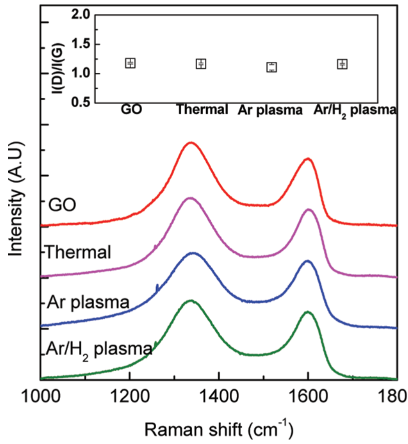

Figure 5. Micro Raman spectra (λ = 633 nm) of GO thin films. Spectra of original GO (red curve), GO reduced by thermal annealing in Ar/H_2 atmosphere (orange curve), GO reduced by Ar plasma (blue curve), and GO reduced by Ar/H_2 plasma (green curve) are shown. In the inset, the $I(D)$:$I(G)$ ratio is shown before and after reduction. All reduction was performed at atmospheric pressure, 150 °C for 30 min.

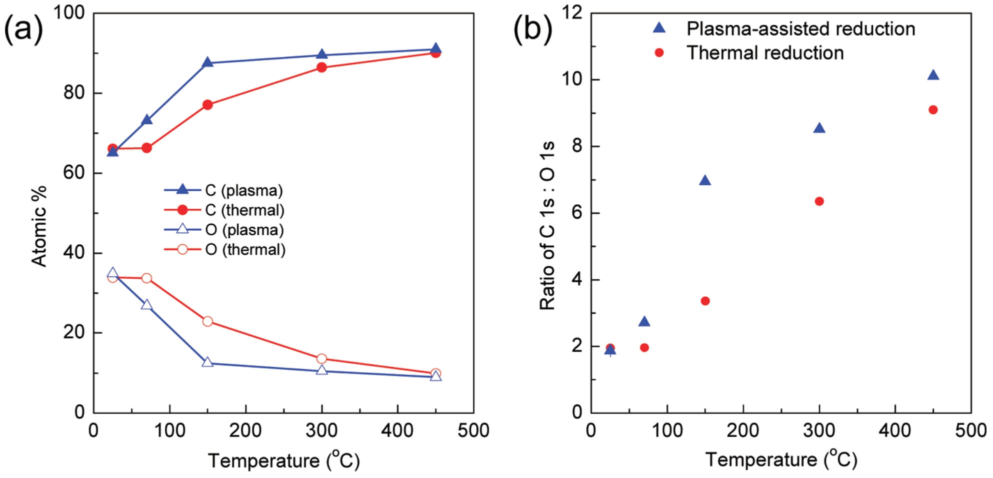

Figure 4. (a) Atomic percentage of C and O and (b) ratio of C 1s:O 1s XPS signal for thermal-reduced and plasma-reduced GO thin films at various temperatures.

Previous reports have shown that reduction by hydrazine hydrate results in a higher I_D/I_G ratio that corresponds to a decrease in the sp^2 cluster size perhaps caused by the creation of defects, vacancies, or distortions of the sp^2 domains due to the removal of oxygen from the graphene sheets.[28,44] In our case, the I_D/I_G ratio before and after reduction remains essentially the same (see inset of Figure 4), indicating that the plasma treatment does not introduce additional defects into the reduced GO film.

To assess the feasibility of our approach for flexible conductor applications, we measured the sheet resistance of GO films reduced on PET. The thickness of the as-deposited films was ~6 μm (Supporting Information), and assuming that the reduction occurs only near the surface, the measurement should be independent of film thickness.[45] Raman spectra of the films indicated that the reduction occurred similarly on PET, as in the case of Au substrates. (See the Supporting Information.) To obtain sheet resistance, we measured the resistance of the reduced films with a two-point probe and applied the following relationship

$$R_s = R\frac{W}{L}$$

where R is the resistance, W is the width, and L is the length between two electrodes. As shown in Table 2, the sheet resistance after plasma-assisted reduction is 4.77×10^4 Ω/sq, which is ~50 times lower than thermal reduction alone (2.14×10^6 Ω/sq) under the same process conditions. The apparent increase in conductivity is most probably due to a higher concentration of sp^2 clusters, which leads to enhanced electrical transport via percolation.[23] Our sheet resistance is comparable to the lowest reported value for hydrazine treatment, followed by thermal annealing (~4.3×10^4 Ω/sq);[5] we note that our process is lower temperature and shorter exposure time. Further improvements in the conductivity may be possible by optimizing the exposure time, discharge current, and sample distance.

We finally address the issue of hydrogenation − the exposure of GO (or reduced GO) to atomic hydrogen suggests that the sp^2 domains in the film could be hydrogenated, similar to what has been observed for graphene.[12] A recent report showed that the mechanism for plasma hydrogenation of graphene is electron irradiation of H_2O adsorbates rather than reaction with atomic hydrogen. Because in our case electrons (and ions) do not interact with the GO film, we do not believe hydrogenation of sp^2 groups occurs. This was verified by a simple test experiment where we treated CVD-grown graphene under typical conditions as our GO and observed no noticeable change in the chemical structure. (See the Supporting Information.) Therefore, we infer that in our process the atomic hydrogen does not react with sp^2 groups in the GO film, and its main chemical pathway is reactions with sp^3 (oxygen functional) groups.

In summary, we have developed and studied a nonequilibrium, plasma-based process for the reduction of GO at low temperature and atmospheric pressure. The generation of atomic hydrogen, as verified by optical characterization of the plasma, results in effective removal of oxygen functional groups in GO films at temperatures as low as 70 °C. The new process conditions demonstrated here open the possibility of reducing GO films by roll-to-roll processing for large-scale, flexible conductor applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional materials analysis. 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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