Electrical current mediated interconversion between graphene oxide to reduced grapene oxide

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In this work, we demonstrate that graphene oxide (GO) can be reversibly converted to reduced-graphene-oxide (rGO) through the use of electric current. Strong electric field could cause ionization of water molecules in air to generate H^+ ions at cathode, causing GO to be reduced. When the bias is reversed, the same electrode becomes positive and OH^- ions are produced. According to Le Chatelier Principle, it then favors the reverse reaction, converting rGO back to GO, $GO+2H^+ +2e^- => rGO + H_2O$. X-ray spectroscopy and Raman spectroscopy were carried to verify the conversion reversibility in the reversed process. © *2011 American Institute of Physics.* [doi:10.1063/1.3580762]

Graphene have researchers intrigued particularly with its high level of carrier mobility and its unique mechanical properties.[1] These properties position graphene as a promising candidate in the field of nanoelectronics. Graphene has been used as electrodes in solar cells,[2] in sensing applications and also transistors.[3] In order to facilitate the use of graphene in these devices, many synthesis methods have been developed. These methods ranged from the usage of chemical vapor deposition[4,5] to solution phase methods that involve chemically exfoliating graphite.[6] However, to synthesize a uniform and large piece of graphene sheet is very challenging.

The reduced form of graphene oxide (rGO) is an alternative to graphene for creating devices that require an electronic band gap. GO can be synthesized via the oxidative treatment of graphite. However, GO is insulating.[7] To recover the high electrical conductivities of GO, it can be chemically reduced to form rGO. A number of approaches to reduce GO have been studied. Examples include thermal,[8] chemical,[9] and electrochemical[10] methods. However, these methods lack controllability in the reduction process, making it challenging to incorporate graphene in nanoelectronic devices. Hence, localized reduction methods and patterning would be important in the design of devices.

To achieve controlled patterning of GO films, various patterning techniques such as laser reduction have been proposed.[11] Recently, it is reported that GO can be reduced through electric current. Not only that electric current can cause GO to be reduced, in this work, we discovered that reoxidation of rGO to GO is also possible by means of an electric current.

GO prepared via Modified Hummer's Method[12] was spin coated on SiO substrate with pre-patterned Au/Cr electrodes for 20s with a speed of 1000rpm. Atomic Force Microscopy (AFM) characterization shows that the thickness of GO was about 65–70nm.

Sweeping electric potential of −1.0 to 1.0 V was applied across a pair of electrodes separated by a distance of 10 μm using Keithley 2636A source-meter for 40 s. A schematic of the measurement setup is shown in Fig. 1(a). The whole process was observed under Cascade Microtech microscope using 50× lens and the entire process was captured by a video camera. The same experiment was repeated using −1.5 V to 1.5 V, −2.0 V till −4.5 V to 4.5 V.

To prepare the sample for X—ray Spectroscopy (XPS) and Raman characterization, a potential of 10 V was applied across a different patterned electrodes of separation 240 μm for approximately 15 min and then a reversed bias of 10 V was applied for another 15 min. The optical image of the patterned electrode for XPS and Raman spectroscopy is shown in supplementary material.[13]

Sweeping voltages varying from −1 to 1 V with increasing magnitude to −4.5 to 4.5 V were applied across the electrodes and optical changes in the sample were recorded by a video camera. The bluish region shown in Fig. 1(c) was caused by electrical reduction. The reduction first took place at cathode (negative electrode) denoted by the appearance of blue color at cathode first. The I-V characteristic was noted for each set of sweeping voltage applied. When the sweeping voltage was increased to 4.5 V, the entire region between the electrodes turns bluish and the current reached the compliance set at 100 nA [see Fig. 1(d)]. It was previously reported that GO could be reduced by means of electric current.[14] The marked increased in the current (reaching compliance of 100 nA) suggested that the GO between the electrodes was reduced. Notably the reduced GO could be defined by the dimension and location of the electrodes, thus achieving controlled patterned reduction in GO.

Figure 1(d) suggest that the size of hysteresis loop increases with the magnitude of sweeping voltage applied. The hysteresis loop could be caused by charged trapping in water molecules from the ambient. After compliance was reached when sweeping potential of 4.5 V was applied, sweeping voltage of 2 V was then applied across the electrodes again and compliance was reached.[13] This suggests the GO has
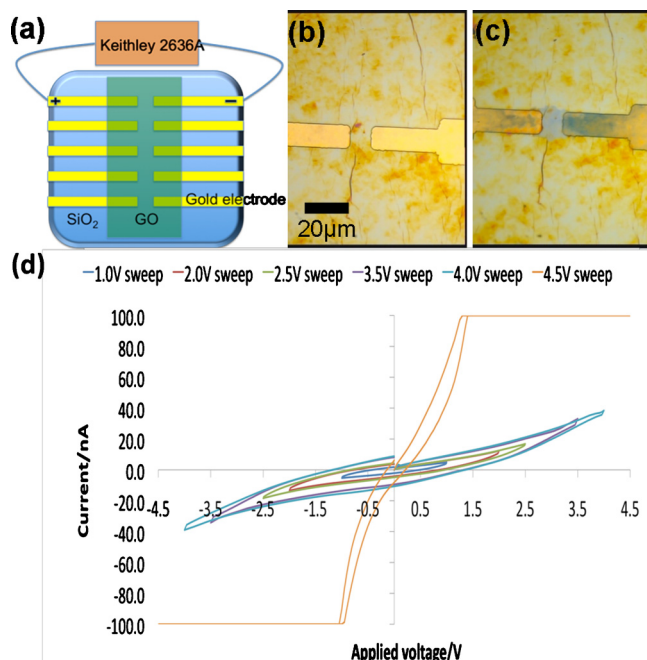
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FIG. 1. (Color online) (a) Schematic diagram of the setup, (b) optical image showing GO before passing 3 V through electrodes, (c) region between the electrodes is fully reduced. Process is no longer reversible. (d) Sweeping voltages varying from 1 to 4.5 V are applied. GO between the electrodes are fully reduced when 4.5 V is applied across the electrodes.
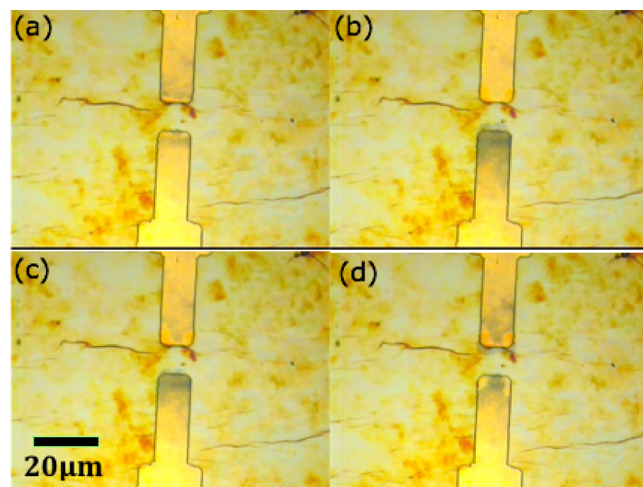

FIG. 2. (Color online) Snapshots at different timings of the color change when sweeping voltage of 3.5 V is applied across the electrodes. (a) 0 s, (b) 15 s, (c) 28 s, and (d) 38 s.

been irreversibly reduced. At the end of the sweeping loop, current did not return to zero suggesting that the sample was charged.

In this work, we had additional discovery that the reduction in GO can be reversed if we controlled the magnitude of the applied bias. Before the entire region between the electrodes turned blue, the color change was reversible when a reversal of voltage bias was applied across the electrodes by reversing the polarities of the electrodes. In this case, the potential applied should not exceed 4 V for this reversibility

to be observed. The process was still reversible after 15 sweeps and it seems that there is no limit to the number of times the process is reversible. Figure 2 shows the snapshots of a 40 s video clip[15] taken when sweeping voltage of −3.5 to 3.5 V was applied across the electrodes. The initial color of GO under the optical microscope is yellowish as shown in Fig. 2(a). At time t=15 s [Fig. 2(b)], blue color emerge from the lower electrode (cathode). When the bias was reversed at 20 s, the blue region started to fade away and emerged from the other electrode. At time t=28 s, the blue region at the lower electrode starts to fade away as shown in Fig. 2(c). In Fig. 2(d), the region around the top electrode became blue. The rate of change in color increased with the potential applied. A 4.5 V potential took about 14 s to completely reduced the area between the electrodes.[15] Once the region between the electrodes was completely converted to blue, the process was no longer reversible.
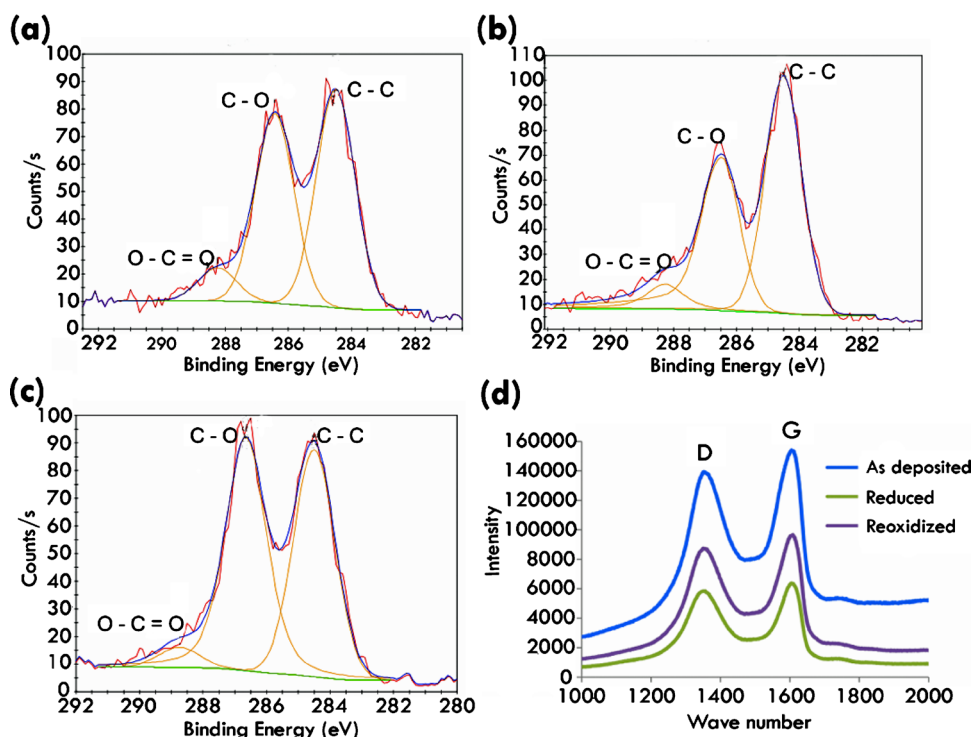

FIG. 3. (Color online) XPS spectral of C 1*s* (a) as deposited before electrical reduction and (b) after electrical reduction. A constant voltage of 10 V is applied for 15 min, (c) electrical reoxidation by reverse bias of 10 V applied for 15 min, and (d) Raman spectroscopy.

TABLE I. Composition of C and O elements. After the reduction by electric pulse, %C in reduced area increases compared to that of unreduced area. After reoxidation by reverse bias, %C in reoxidized area increases compared to the reduced area but is still less than unreduced area.

Elements	As deposited	Reduced area	Reoxidized area
C	64.5	71.5	61.7
O	35.5	28.5	38.3

TABLE II. Relative area intensity ratio of C 1s normalized to C—C peak.

	Unreduced area intensity ratio normalized to C—C	Reduced area intensity ratio normalized to C—C	Reoxidized area intensity ratio normalized to C—C
C—C	1.0	1.0	1.0
C—O	0.9	0.8	1.1
O—C=O	0.2	0.1	0.1

To further investigate the reversible conversion GO and rGO, XPS and Raman studies were carried out on the sample. Figures 3(a)–3(c) shows XPS spectra obtained. They correspond to the XPS spectra obtained before electrical reduction Fig. 3(a), after complete electrical reduction Fig. 3(b) and electrical reoxidation Fig. 3(c). The binding energy of C—C bond is assigned to be around 284.5 eV and C—O and O—C=O have binding energies around 286.9 and 288.3 eV. The binding energies for C—O and C=O are located around 532.4 eV and 530.9 eV, respectively (see Ref. 13). The error bound for the data obtained is 0.2 eV. As evident from XPS data, the relative peak area intensity of C—O to C—C decreases after electrical reduction and increases again when the bias is reversed.

Table I shows the percentage composition of carbon and oxygen elements in the sample before reduction, after reduction and reoxidation as calculated by XPS manufacturer software. The composition of C increases when it is reduced and decreases after reoxidation. The amount of oxygen atoms after reoxidation is more than the initial unreduced GO.

Table II shows the relative area intensity ratios of C—C to C=O and O—C=O. After reduction by electric current, peak areas of both C—O and O—C=O in the reduced area decrease compared to that of unreduced area. This shows that reduction in C—O and O—C=O did take place by electric current. After reoxidation by applying reverse bias, peak area of C—O in reoxidized area increases compared to the reduced area. XPS characterization indicates a restoration of rGO back to GO.

It is also important to take note that C=O bonds is not recovered during the reoxidation process. In addition, O 1s spectra show the intensity of O=C decreases after reduction but cannot be recovered back after the reverse current. Hence, it is in agreement with C 1s spectra results.[13]

It is known that Raman is a powerful tool in the characterization of graphene and GO. In Fig. 3(d), the results display D and G peak intensities at 1355 cm^{-1} and 1591 cm^{-1}, respectively.

After electric reduction, the D and G band peaks become slightly sharper. There is no major band shift in the Raman spectrum. The I_D/I_G ratio increases from 0.90 to 0.93 after electrical reduction and decreases back to 0.91 after reverse bias is applied. It has been reported that the intensity of D-band increases when GO is reduced.[16] This increase is due to an increase in the number of carbon edge-atoms during the reduction, creating new small size graphitic domain that is generally the structural change after GO is reduced. Hence, the Raman result obtained is in agreement with the results previously reported.

The reduction process always occurs at cathode (negative electrode). The strong electric field could cause ionization of the water molecules in air to give H^+ ions at cathode and OH^- ions at anode. It was reported that H^+ ions is important and play a role in reduction in GO. The cathode reaction can then be represented by the half equation GO $+2H^+ + 2e^- = > rGO + H_2O$. However, when the bias is reversed, the same electrode now becomes the positive electrode and OH^- ions are produced. The OH^- ions remove H^+ ions, causing a decrease in the concentration of H^+ at the electrode. According to Le Chatelier's Principle, it then favors the reverse reactions, converting rGO back to GO.

The reversible conversion of GO to rGO can be achieved using electric current. This result is further verified by XPS and Raman characterization. Both the results show good restoration of rGO back to GO when reverse bias is applied.

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