30-Inch Roll-Based Production of High-Quality Graphene Films for Flexible Transparent Electrodes

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We report a chemical vapor deposition (CVD) synthesis of ultra-large area monolayer graphene films and roll-based layer-by-layer transfer onto flexible substrates. The monolayer shows the sheet resistance as small as ~125 Ω/sq with 97.4% optical transmittance and a unique half-integer quantum Hall effect indicating the high-quality of graphene films. The 30-inch scale multiple roll-to-roll transfer further enhance the electrical properties of the graphene films, resulting in ~40 Ω/sq sheet resistance and ~90 % transparency comparable to recent commercial transparent electrodes such as indium tin oxides (ITO).
Graphene and related materials have attracted tremendous attention for the last a few years due to their fascinating electrical (1), mechanical (2, 3), and chemical (4, 5) properties. There have been many efforts to utilize these outstanding properties of graphene for macroscopic applications such as transparent conducting films useful for flexible/stretchable electronics (6-8). However, the lack of efficient synthesis, transfer, and doping methods limited the scale and the quality needed for the practical production of graphene films. For example, a conventional transparent electrode, indium tin oxides (ITO), that are commonly used in solar cells, touch sensors and flat panel displays show a sheet resistance smaller than 100 Ω/sq with ~90% optical transparency as well as unlimited scalability, while the best records of graphene has still remained around ~500 Ω/sq sheet resistance, ~90% transparency, and a few centimetre scale at the moment (6, 9-11).

On the other hand, typical CVD methods inevitably require a rigid substrate that can stand high temperatures close to ~1000 °C and an etching process for removing metal catalyst layers, which are main obstacles for the direct use of graphene on as-grown substrates. Therefore, the transfer of graphene films onto a foreign substrate is essential. However, the transferrable size of graphene has been limited below a few inches scale due to the size limit of rigid substrates and the inhomogeneous reaction temperature inside a CVD furnace. This can be overcome by using roll-type metal foils fitting the tubular shape of the furnace. In addition, the flexibility of graphene and Cu foils allow efficient etching and transfer processes employing a cost and time-effective roll-to-roll production system.

There are three essential steps in the roll-to-roll transfer (12-14) (Fig. 1A), which are i) adhesion of polymer supports to the graphene on a Cu foil, ii) etching of Cu
layers, and iii) release of graphene layers and transfer on to a target substrate. In the adhesion step, the graphene film grown on a Cu foil is attached to a thin polymer support such as thermal-release tapes between two rollers. In the subsequent step, the Cu layers are removed by electrochemical reaction with a Cu etchant (6, 9-11). Finally, the graphene films are transferred from the polymer support onto a target substrate by removing the adhesive force on the polymer support. In the case of using thermal release tapes (15), the graphene films are detached from the tapes and released to counter substrates by thermal treatment (Fig. 1A).

Fig. 2 shows the photographs of roll-based synthesis and transfer processes. An 8-inch wide tubular quartz reactor is employed in the CVD system, where monolayer graphene films can be synthesized on a roll of Cu foil as large as 30-inch in diagonal direction (Fig. 2A). Usually, there exists temperature gradient depending on the radial position inside a tubular reactor. This sometimes results in inhomogeneous growth of graphene on Cu foils. To solve this problem, ~7.5-inch quartz tube wrapped with a Cu foil is inserted and suspended inside the 8-inch quartz tube. Thus, the radial inhomogeneity in reaction temperature can be minimized. In the first step of synthesis, the roll of Cu foil is inserted to a tubular quartz tube and then heated up to 1000°C with flowing 10 sccm H_2 at 180 mTorr. After reaching 1000°C, the sample is annealed for 30 min without changing flow rate and pressure. During this annealing process, the single-crystalline grain sizes of Cu foils are increasing from a few µm to ~100 µm scales, leading to the higher quality of graphene films (16). The gas mixture of CH_4 and H_2 is then flowed at 1.6 Torr with a rate of 30 sccm and 10 sccm for 15 min, respectively. Finally, the sample is rapidly cooled down to room temperature (~10°C/sec) with flowing H_2 under the pressure of 180 mTorr.
After the growth, the graphene film grown on the Cu foil is attached to a thermal release tape (Nitto Denko Co.) by applying soft pressure (~0.2 MPa) between two rollers. After etching the Cu foil in a plastic bath filled with etching solution (19), the transferred graphene film on the tape is rinsed with DI water to remove residual etchant, and it is ready to be transferred to any kinds of flat or curved surfaces on demand. Subsequently, the graphene film on the thermal release tape is inserted to the rolls together with a target substrate and exposed to mild heat of 90–120°C for 3–5 min, resulting in the transfer of graphene films from the tape to the target substrate (Fig. 2B). By repeating these steps on the same substrate, multilayered graphene films can be prepared, showing enhanced electrical and optical properties as we will discuss later. Fig. 2C shows the 30-inch multilayer graphene film transferred a roll of 130 μm thick polyethylene terephthalate (PET) substrates. The scalability and the processibility of CVD and roll-to-roll methods are expected to enable the continuous production of graphene films in large scale.

The Raman spectra show that the graphene films synthesized on Cu foils are dominantly monolayers with small D-band peaks indicating the high-quality of graphene structures (Fig. 3A). As the number of layers increases, the intensities of G and 2D band peaks are increasing together, but their ratios don’t change significantly, which is clearly different from the case of multilayer graphene exfoliated from graphite crystals (17, 18). This is because the hexagonal lattices of upper and lower layers are randomly oriented unlike graphite so that the original properties of each monolayer remain unchanged even after staking into multilayers (19, 20). Therefore, we expect that the sheet resistance is proportional to the number of stacked graphene layers. The
optical transmittance is usually decreased by 2.2~2.3% for an additional transfer, indicating that the transferred film is mostly a monolayer (6, 21).

The electrical properties of graphene films formed through layer-by-layer staking methods are investigated. Usually, the sheet resistance of the graphene film with ~97% transmittance is as low as ~125 Ω/sq when it is transferred by a soluble polymer support such as polymethyl-methacrylate (PMMA) (9-11). However, the transferrable size of the wet transfer methods is limited below a few centimetres because of the weak mechanical strength of spin-coated PMMA layers (6, 9-11, 22), while the scale of roll-to-roll dry transfer assisted by a thermal release tape is in principle unlimited.

In the process of roll-to-roll dry transfer, the first layer usually shows ~2 times larger sheet resistance than the case of the PMMA-assisted wet transfer method. As the number of layers increases, the resistance drops faster compared to the wet transfer method (Fig. 4A). We suppose that the adhesion of the first layer with the substrate is not strong enough for the complete separation of graphene films from thermal release tapes. As a result, there can be mechanical damages on graphene films, leading to the increase of overall sheet resistance. Since additional layers are not directly affected by the adhesion with substrate surface, the sheet resistance of multilayers prepared by the roll-to-roll method doesn’t differ much from the wet transfer case.

Standard e-beam lithography has been used to fabricate graphene hall bars on conventional 300nm SiO₂/Si (Fig. 4C). The left panel of Fig. 4C shows the four terminal resistance measurement as a function of back-gate voltage ($V_{bg}$) at room temperature and zero magnetic field of such samples. We observe the graphene specific gate bias dependence of the resistance showing sharp Dirac peaks and large field effect mobilities of 4,000~12,000 cm²/Vs, indicating the high quality of our CVD-grown
graphene. This allows the observation of the quantum Hall effect at 3K with applying a magnetic field $B=9$T (Fig. 4C, right). The fingerprint of single layer graphene, the half-integer quantum Hall effect is observed with plateaus at filling factor $\nu=2$, 6, and 10 at $R_{xy}=1/2$, 1/6 and 1/10($h/e^2$), respectively.

In summary, we have demonstrated a promising route to synthesize and transfer ultra-large-area graphene films that are highly conducting and transparent, based on roll-to-roll processes. The multiple transfer of graphene films considerably enhance the electrical/optical properties, comparable to those of commercial grade transparent electrodes. Considering the outstanding scalability/processibility of roll-to-roll and CVD methods and the extraordinary flexibility/conductivity of graphene films, we expect the commercial production and application for large-scale transparent electrodes replacing the use of ITO can be realized in near future.

References and Notes

1. A. K. Geim, K. S. Novoselov, Nat. Mater. 6, 183-191 (2007).
2. C. Lee, X. Wei, J. W. Kysar, J. Hone, Science 321, 385-388 (2008).
3. J. S. Bunch et al., Nano Lett. 8, 2458-2462 (2008).
4. D. C. Elias et al., Science 323, 610-613 (2009).
5. X. Wang, et al., Science 324, 768-771 (2009).
6. K. S. Kim et al., Nature 457, 706-710 (2009).
7. D. H. Kim et al., Science 320, 507-511 (2008).
8. T. Sekitani et al., Science 321, 1468-1472 (2008).
9. A. Reina et al., Nano Lett. 9, 30-35 (2009).
10. X. Li et al., Science 324, 1312-1314 (2009).
11. A. Reina et al., Nano Res. 2, 509-516 (2009).
12. S. H. Ahn, L. J. Guo, Adv. Mater. 20, 2044-2049 (2008).
13. R. Yerushalmi, Z. A. Jacobson, J. C. Ho, Z. Fan, A. Javey, App. Phys. Lett. 91, 203104. (2007).
14. Y. K. Chang, F. C. Hong, Nanotechnology 20, 195302 (2009).
15. Y. B. Lee et al., arXiv:0910.4783 (2009).
16. Materials and methods are available in supporting material.
17. D. S. Lee et al., Nano Lett. 8, 4320-4325 (2008).
18. Q. Li, Z. Lin, M. Chun, Y. Fang, Nano Lett. 9, 2129-2132(2009).
19. X. Li et al., Nano Lett. Article ASAP, DOI: 10.1021/nl902623y (2009).
20. Z. Li, Y. Wang, T. Yu, Y. You, Z. Shun, Phys. Rev. B 77, 235403 (2008).
21. R. R. Nair et al., Science 320, 1308 (2008).
22. H. Cao et al., arXiv:0910.4329 (2009).
23. H.-Z. Geng et al. J. Am. Chem. Soc. 129, 7758-7759 (2007).
24. J.-Y. Lee, S. T. Connor, Y. Cui, P. Peumans. Nano Lett. 8, 689-692 (2008).
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Fig. 1. Schematic of the roll-based production of graphene films grown on a Cu foil, including adhesion of polymer supports, Cu etching (rinsing), and dry transfer-printing on a target substrate. A wet chemical doping can be carried out using the similar set-up used for etching.
Fig. 2. Photographs of the roll-based production of graphene films. (A) A Cu foil wrapping around a 7.5-inch quartz tube to be inserted into an 8-inch quartz reactor. The lower image shows the Cu foil reacting with CH₄ and H₂ gases at high temperatures. (B) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film at 120°C. (C) A transparent ultra-large-area graphene film transferred on a 35-inch PET sheet.
Fig. 3. Optical characterizations of the graphene films prepared by layer-by-layer transfer on SiO$_2$/Si and on PET substrates. (A) Raman spectra of graphene films with different number of stacked layers. The left inset shows a photograph of transferred graphene layers on a 4-inch SiO$_2$(300nm)/Si wafer. The right inset is a typical optical microscope image of the monolayer graphene, showing >95% monolayer coverage. A PMMA-assisted transfer method is used for this sample. (B) UV-Visible spectra of layer-by-layer transferred graphene films on quartz substrates.
Fig. 4. Electrical characterizations of layer-by-layer transferred and HNO$_3$-doped graphene films. (A) Sheet resistances of transferred graphene films using a roll-to-roll dry transfer method combined with thermal release tapes and a PMMA-assisted wet transfer method. (B) Comparison of sheet resistance vs. transmittance plots from previous reference. The scheme is borrowed from Ref. 19. (C) Electrical properties of a monolayer graphene hall bar device. Room temperature four-probe resistance is measured as a function of gate voltage of a monolayer graphene Hall bar shown in the insert (left). QHE effect at 3K and 9T is measured from the same device (right). The longitudinal magnetoresistance $R_{xx}$ and transverse magnetoresistance $-R_{xy}$ are plotted as a function of gate voltage. The first three half-integer plateaus at $v = 2, 6,$ and $10$, typical for single layer graphene are clearly seen.
Supporting Material

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A. Enlarged grain sizes of Cu foil after annealing/growth

Fig. S1. Grain size analyses of Cu foils before and after annealing/growth. (A) Optical microscope images of Cu foils before and after graphene growth at 1,000°C. The cracks on foils usually formed at grain boundaries. (B) Optical images of polished Cu foils before and after annealing at 1,000°C, followed by brief acid treatment. The grain boundaries are etched faster than single crystalline surfaces, resulting in the formation line patterns on the polished Cu surface.