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Metal-assisted exfoliation (MAE): green, roll-to-roll compatible method for transferring graphene to flexible substrates

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Abstract

Graphene is expected to play a significant role in future technologies that span a range from consumer electronics, to devices for the conversion and storage of energy, to conformable biomedical devices for healthcare. To realize these applications, however, a low-cost method of synthesizing large areas of high-quality graphene is required. Currently, the only method to generate large-area single-layer graphene that is compatible with roll-to-roll manufacturing destroys approximately 300 kg of copper foil (thickness = 25 μm) for every 1 g of graphene produced. This paper describes a new environmentally benign and scalable process of transferring graphene to flexible substrates. The process is based on the preferential adhesion of certain thin metallic films to graphene; separation of the graphene from the catalytic copper foil is followed by lamination to a flexible target substrate in a process that is compatible with roll-to-roll manufacturing. The copper substrate is indefinitely reusable and the method is substantially greener than the current process that uses relatively large amounts of corrosive etchants to remove the copper. The sheet resistance of the graphene produced by this new process is unoptimized but should be comparable in principle to that produced by the standard method, given the defects observable by Raman spectroscopy and the presence of process-induced cracks. With further improvements, this green, inexpensive synthesis of single-layer graphene could enable applications in flexible, stretchable, and disposable electronics, low-profile and lightweight barrier materials, and in large-area displays and photovoltaic modules.

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(Some figures may appear in colour only in the online journal)

1. Introduction

The only current method for growing large-area single-layer graphene that is compatible with roll-to-roll manufacturing is highly wasteful [1]. Efforts to reduce this waste have been driven by two goals. The first goal is to reduce the cost and environmental impact for relatively high-end applications—i.e., nanoelectronics [2, 3] and transparent electrodes [4]—for

which graphene is currently regarded as an important future component. The second goal is to enable potential applications—i.e., disposable electronics [5], textiles [6, 7], conformable biomedical devices [8], and thin-film photovoltaic modules [9, 10] (which will need to cover thousands of square kilometers)—that would be difficult to realize using graphene at its current cost. In the well-known, roll-to-roll-compatible process originally described by Bae *et al*, single-

layer graphene was grown on large-area copper foils by chemical vapor deposition (CVD) and released onto a carrier substrate by chemical etching of the copper [4]. This process is significant in its ability to produce films over relatively large areas, but the cost of a one-atom-thick layer of graphene includes the destruction of an equal area of a 10^5 -atom-thick copper foil, along with the economic costs and environmental externalities associated with preparing the copper substrates for synthesis and handling large amounts of corrosive waste.

There exists another issue that precludes the manufacturing of graphene on an industrial scale besides the high costs of graphene production. Generating sufficient amounts (square kilometers) of graphene the industries that can best utilize its properties—as a barrier material or as a transparent conductive electrode—requires a robust process capable of high production yields. The production rate for the above-mentioned process is limited by the need to prepare each batch of copper foil prior to graphene synthesis (extensive cleaning, electropolishing, and annealing) as well as the need for the prolonged etching of the copper foil in order to liberate graphene. Both steps amount to more than an hour of additional processing time for a given batch, besides significantly adding to the cost of the product. Reusing the copper substrate by non-destructive removal of graphene from its surface would not only substantially increase the attainable production rate by removing the necessity of priming and etching the copper substrates, but would also make it possible to double the graphene yield per batch due to the ability to remove graphene on both surfaces of the foil. This paper describes a process that is amenable to large-area production of single-layer graphene by mechanical exfoliation. We believe the process could be performed at rates of production that are required for manufacturing.

2. Experimental design

Our process is based on the differential adhesion of graphene to various metals, subsequent mechanical exfoliation, and lamination to a flexible substrate using a thermally deactivated adhesive (each step of the process is depicted in figure 1). We have nicknamed the process metal-assisted exfoliation—‘MAE’. A similar technique has been previously used to exfoliate graphene from single-crystalline wafers [11] bearing hydrogen-terminated germanium using gold as the ‘adhesive’ metal [12] but to our knowledge such attempts have been limited to graphene transferred from the perfect surfaces of wafers and to their dimensions, and this is the first time that MAE is demonstrated for graphene grown on copper. The process appears to be applicable to large-area (limited by the reactor and metallization chamber dimensions) graphene transfer from relatively rough surfaces. In brief, single-layer graphene was grown on a copper foil by ambient-pressure CVD (step 1). A 150 nm film of nickel (or cobalt) was deposited on the graphene by physical vapor deposition (step 2 and figure 2(a)). Thermal release tape was applied (step 3 and figure 2(b)); peeling up the thermal release tape exfoliated the metal/graphene bilayer films from the copper

substrate (step 4 and figure 2(c)), which was reusable without further treatment. Lamination of the graphene to a commercial polyethylene terephthalate (PET) substrate, bearing a thermoplastic adhesive coating, at 100 °C deactivated the adhesive on the thermal release tape, and the graphene remained on the plastic substrate (step 5 and figures 2(d), (e)). The sheet containing PET/graphene/metallic film was then dipped into the bath containing a metal etchant solution for 3–5 s (step 6 and figure 2(f)) and rinsed in deionized water to yield a sheet of PET covered with single-layer graphene (step 7 and figures 2(g) and (h)).

Even though vacuum metallization techniques are generally perceived in academia as being costly, such techniques have been used for many decades to produce thousands of square kilometers of such commodities as potato-chip bags, magnetic tapes, capacitors and optical films. Such systems reach web-speeds of meters per second, deposition rates of hundreds of micrometers per minute, and annual production of millions of square meters [13]. Additionally, alternative, ambient pressure graphene metallization techniques such as nickel electro(less)-deposition that could further increase the production rate and decrease its cost are currently under investigation.

The final receiving substrate—PET—was selected for its widespread use in flexible electronics. Additionally, the commercially available PET films used in the lamination process bear a thermoplastic layer that adheres well to graphene and facilitates its transfer from the thermal release tape. We successfully exfoliated graphene from the copper foil using thin films of nickel, cobalt, and gold. A comparative density-functional study of the binding energies between graphene and various metal surfaces by Hamada and Otani revealed a stronger preference of graphene to nickel (141 meV) than to copper (62 meV) [14]. The strong adhesion of nickel to graphene was also exploited by Kim *et al* in a two-step exfoliation of graphene from SiC surfaces, but this process is not likely to be compatible with roll-to-roll manufacturing, because of the inflexibility of the SiC wafers [15]. In addition to the metals listed above, we also attempted MAE with iron and aluminum, but found they did not exhibit preferential adhesion to graphene and thus did not enable exfoliation of graphene from the copper substrate. Of the three metals that enabled exfoliation, only nickel and cobalt could be etched without damaging the graphene (i.e., by etching it or rendering it non-conductive). For example, etching gold with the standard solution containing iodine and potassium iodide rendered the graphene non-conductive.

3. Results and discussion

To determine the quality of the graphene transferred by our method, we measured the sheet resistance (R_s) and the ratio of the D/G peak from the Raman spectra. We obtained values of R_s that varied within an order of magnitude between samples. We attribute the variability, in part, to the manual nature of the transfer of the nickel/graphene or cobalt/graphene bilayer films to the thermal release tape and the subsequent

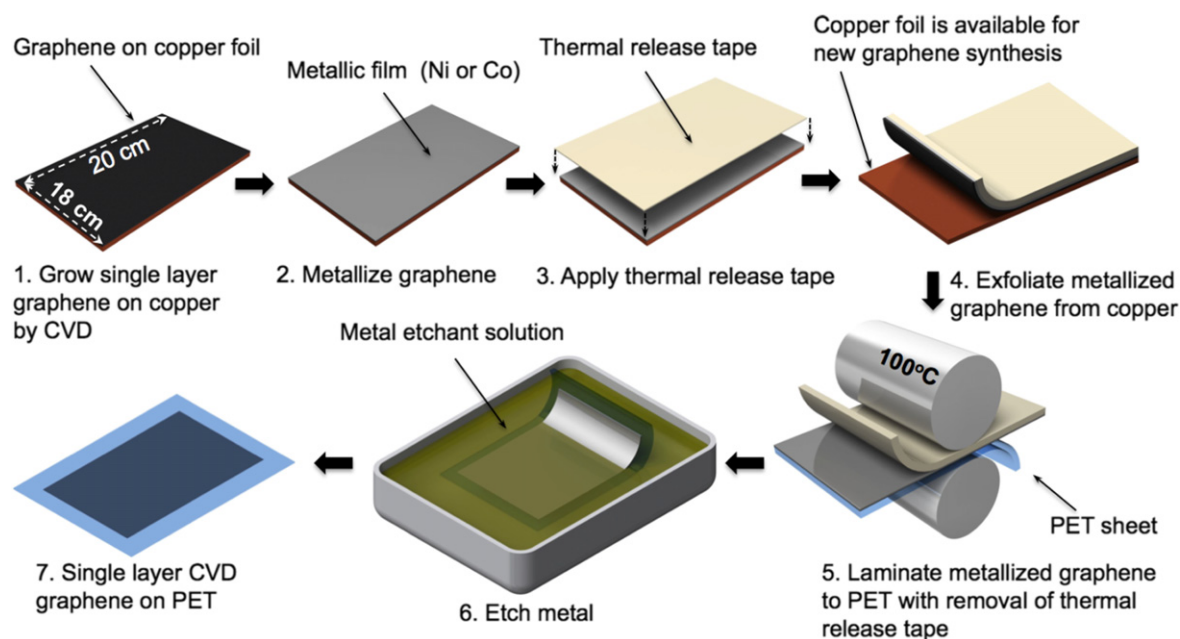


Figure 1. Summary of the MAE process: large-area transfer of single-layer graphene from catalytic copper substrates to PET sheets. The process is based on preferential adhesion of nickel (or cobalt) to graphene, exfoliation, and lamination mediated by tape with a thermally deactivated adhesive.

mechanical damage to the film due to the hot-press lamination of the composite to PET at 100 °C. The lowest value of R_s we obtained was $163 \, \Omega \text{ sq}^{-1}$ compared to the lowest value of $325 \, \Omega \text{ sq}^{-1}$ obtained from graphene transferred using the standard method in which the copper was etched. This low observed resistance is possibly due to doping of the graphene surface with metals (nickel, iron) or their chlorides [16], as we did not perform any other post-processing of the MAE transferred graphene following the etching of the nickel film in iron (III) chloride besides rinsing in deionized water (three times, 5 min each). We also observed cracks in the nickel film after exfoliation (figures 2(c), 3), which we attribute, again, to the manual nature of the exfoliation step, along with the inability of the nickel or cobalt film to accommodate the tensile strain imposed on it during the peeling process. These cracks, which probably propagated through the graphene (figure 2(h)), produced an anisotropic sheet resistance; the average R_s measured parallel to the cracks ($850 \pm 250 \, \Omega \text{ sq}^{-1}$) was an order of magnitude lower than when measured perpendicular to the cracks ($8000 \pm 2000 \, \Omega \text{ sq}^{-1}$). The cracks formed mostly orthogonally to the peeling direction with their density highest at the starting point of the exfoliation (about three cracks per mm), where the radius of curvature of the films was the smallest and the metallic films were subject to greatest tensile stress, to the average of 0.7 cracks per mm throughout the major area of the film, where the radius of curvature was mostly constant throughout the process of exfoliation. It is important to note that the formation of cracks is not intrinsic to the MAE and can be mitigated. For example, relatively large areas of metallized graphene can be exfoliated directly, without additional supporting films or other structures. Such exfoliated films tend to scroll up due to the inherent stresses in evaporated thin films and are difficult

to handle but display no cracking behavior over the entire observed area (about 1 cm^2). The absence of cracking can be explained by the thinness of the films sandwich as compared to that where the films are supported by thermal release tape. Being about 1000 times thinner, the freestanding films allow 1000 times smaller bending radii. An automated process, where the metallized graphene film is subject to reduced tensile strain by using rollers with large radii of curvature, or by using a stiffer adhesive, should reduce the occurrence of cracking or help avoid it altogether. It is possible that kinetically controlled transfer printing by a reusable stamp, as described by Rogers and coworkers, would permit transfer without using thermal release tape [17].

The metal thickness of 150 nm was found to be optimal for the MAE process as it supported complete graphene removal while being thin enough to allow fast processing times. Thicknesses of 10, 20, and 50 nm achieved partial to complete graphene removal from copper but appeared to not be robust enough for the MAE process and resulted in severely degraded transferred films. Thicker films of 1 and $2 \, \mu\text{m}$ (150 nm were evaporated and 850 and 1850 nm were electroplated) were also explored. While these thick films made direct (unsupported) exfoliation of metallized graphene from copper more productive (greater areas of graphene could be peeled off with tweezers), the large-area MAE transfer utilizing these films still produced the anisotropic cracking, albeit of a lower density (~ 0.3 cracks per mm).

The Raman spectra of the graphene as grown on copper and after exfoliation are shown in figures 4(a) and (b). The spectra reveal the complete removal of graphene from copper in the exfoliated region as also supported by optical microscopy studies of the residual material on copper (figure 6(d)). To determine the capacity of a given metal to support MAE of

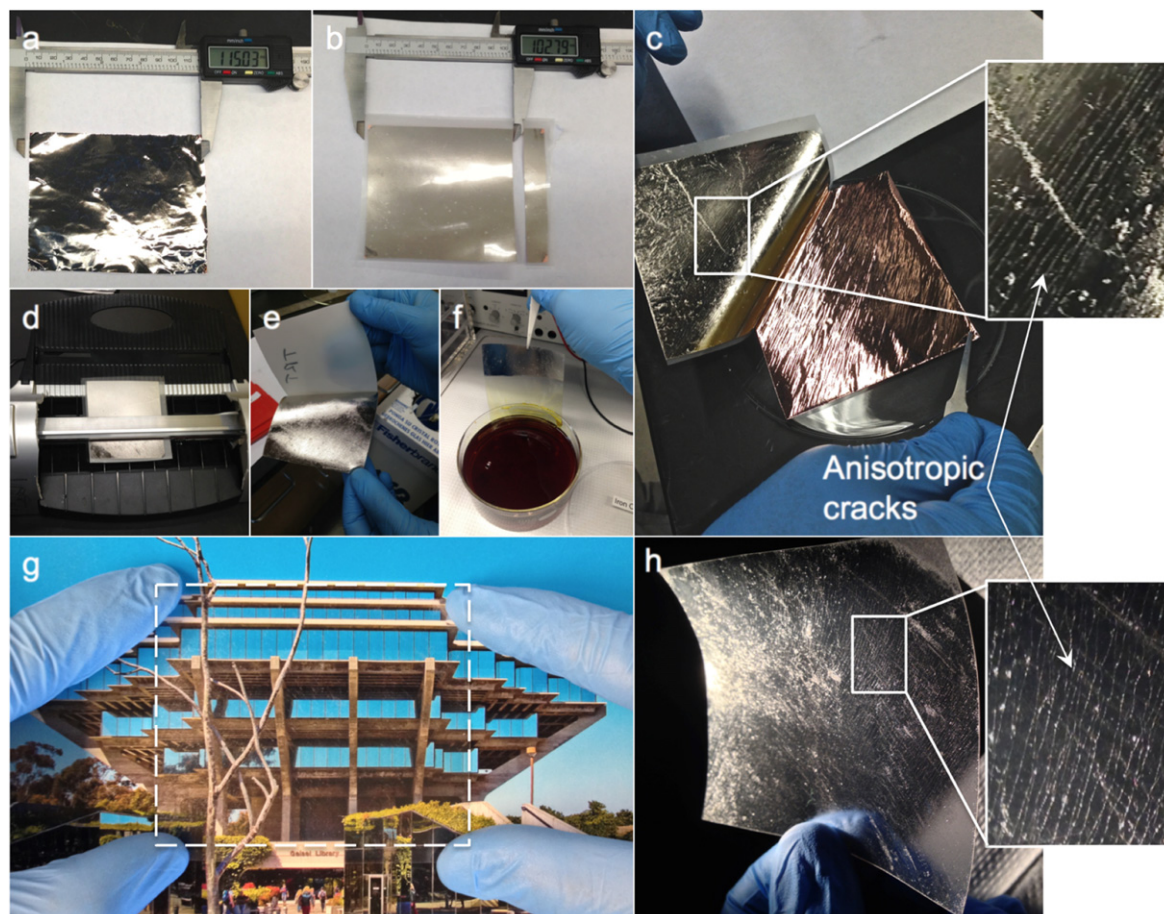


Figure 2. Photographs of the consecutive steps of the MAE of graphene. Single layer graphene on a copper foil after: (a) metallization with nickel, (b) application of thermal release tape, (c) peeling metallized graphene off of the copper foil, (d) lamination of a PET sheet to the metallized graphene (with concomitant deactivation of the thermal release tape), (e) removal of the thermal release tape from the PET/graphene/nickel sheet, (f) dipping the PET/graphene/nickel sheet into the iron (III) chloride solution (3–5 s). The PET sheet coated with single-layer graphene (g) is shown against a postcard depicting the UCSD Geisel library (the outline of the PET/graphene sheet is indicated by the dashed rectangle). An image (h) is also shown of the PET/graphene sheet illuminated at a grazing angle to highlight the cracks that form perpendicular to the peeling of the thermal release tape/metallic film/graphene sheet from the copper foil (shown in detail in the insets of (c) and (h)).

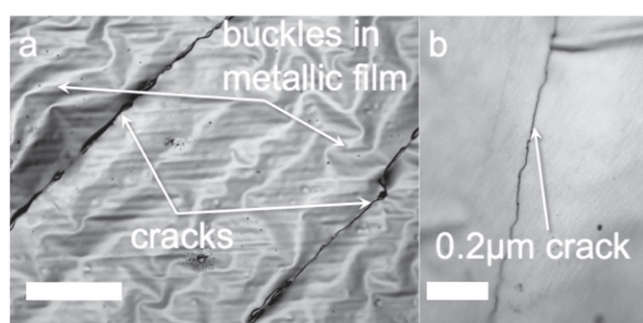


Figure 3. Optical micrograph of cracks in the nickel film after MAE of graphene from copper at 200 \times magnification ((a), scale bar 100 μ m) and at 1000 \times magnification ((b), scale bar 10 μ m). The cracks range in width from tens of nanometers to 1.5 μ m.

graphene from copper, we compared the spectra of the metallic films of gold, cobalt, and nickel after exfoliation of graphene (figures 4(c), (e), and (g)) to the spectra of the respective bare metallic films (figures 4(d), (f), and (h)). The appearance of the peaks characteristic of graphene (D, G, and

2D, highlighted in yellow) on the spectra (figures 4(c), (e), and (g)) revealed the presence of graphene on the films after exfoliation; this observation demonstrated the removal of graphene from copper. We noticed that graphene exfoliated with gold (figure 4(c)) exhibited a smaller D peak than that of graphene transferred with cobalt and nickel (figures 4(e), (g)); this observation suggests that gold is less damaging to graphene, possibly because of the chemical inertness of gold. Figure 5 provides a direct comparison of the defects present in the graphene produced by the prevailing method of wet-transfer described by Bae *et al* to that produced by the MAE process [4]. To obtain these spectra, the graphene produced by both processes was laminated to a Si/SiO₂ substrate. For the traditional wet-transfer, this was achieved by spin-coating poly(methylmethacrylate) (PMMA) on top of graphene and etching the copper substrate. For the Raman spectroscopy of the MAE sample, epoxy was cured on top of the metallized graphene and it was then peeled off of the copper foil. We then spin-coated PMMA on top of the exposed surface of graphene and etched the underlying nickel film in FeCl₃. The

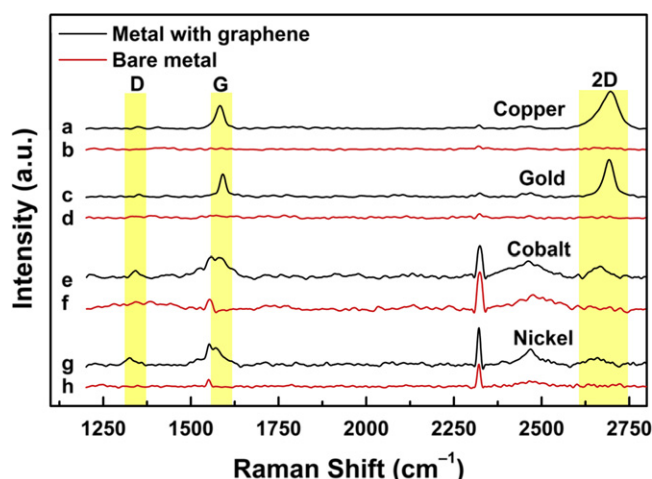


Figure 4. Representative Raman spectra of graphene ‘as grown’ on copper foil (a), copper foil after metal-assisted graphene exfoliation (b) (no graphene peaks indicate a complete graphene removal from the copper foil), graphene on metallic films transferred by MAE from copper ((c), (e), (g)) and the pure metal films respectively ((d), (f), (h)) (gold and copper substrates significantly enhance the Raman scattering and produce strong, well-defined graphene peaks—highlighted in yellow—as compared to cobalt and nickel). The baseline in the spectra has been ‘flattened’ by curve-fitted subtraction.

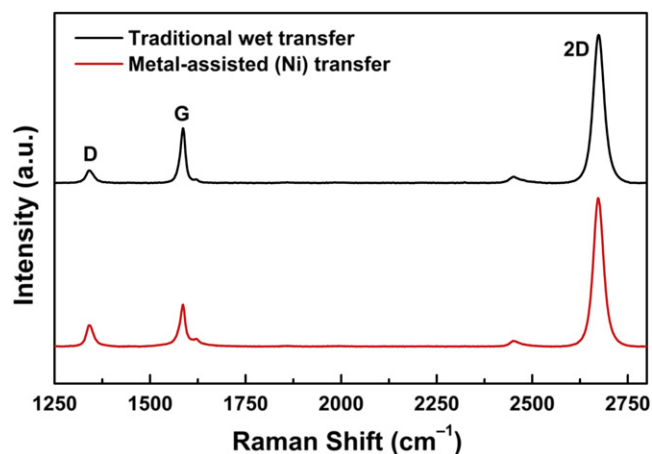


Figure 5. Raman spectra of graphene transferred to Si/SiO₂ by traditional wet-transfer method (black) and metal-assisted (Ni) method (red).

freestanding graphene/PMMA was then transferred to DI water three times before applying it to the Si/SiO₂ wafer chip. The PMMA was then removed by submersion in a boiling acetone bath.

The quality of graphene was judged on the basis of the ratio of the D/G (at 1330 cm⁻¹ and 1580 cm⁻¹) and 2D/G peaks (at 2700 cm⁻¹ and 1580 cm⁻¹) in the Raman spectra [18]. The observed 2D/G ratio of our graphene was equal to or greater than 2.8 for all measurements; this ratio is consistent with the presence of single layer graphene [18]. Compared to the traditional wet-transfer process, the D/G peak ratio in the MAE process was increased by a factor of two (from 0.23 for wet-transfer to 0.50 for MAE). It is possible that the increase in the D-peak in the graphene

transferred by the MAE process is due to damage during the electron-beam evaporation of the nickel film, mechanical damage during the metal-assisted exfoliation, as well as damage during the following wet-transfer process. We expect that other metallization techniques such as electro- or electroless deposition of nickel could be less damaging to the graphene.

The environmental benignity of the MAE process is predicated on the reusability of the copper foil used to grow the graphene. To determine the impact of reusing the same copper substrate on the growth of graphene, we investigated the quality of the graphene grown on copper after cyclic growth and transfer. Remarkably, the quality of the graphene increased after successive cycles of growth (figures 6(a)–(c), (e)). We hypothesize that the increase in quality might be because of the additional annealing of the copper substrate during each cycle of graphene synthesis as well as the removal of surface contaminants with each metal-assisted graphene exfoliation, which produced a cleaner surface for subsequent growth (after each graphene exfoliation, the copper foil substrate was immediately placed into the CVD reactor chamber under high vacuum to avoid contamination of the surface).

In order to demonstrate that the MAE process completely exfoliates graphene from the copper foil, all material remaining on the copper foil after exfoliation of graphene was transferred onto a Si/SiO₂ wafer using the traditional wet-transfer process for optical microscopy (figure 6(d)). Also, the Raman spectra taken on the copper surface immediately after the MAE revealed no graphene peaks (figure 4(b)). The presence of only sporadic, small residual individual graphene grains on the copper foil following MAE indicates that this process transfers predominantly the continuous top (metalized) layer of graphene and supports the theory that small patches of a second graphene layer form beneath the first layer during graphene growth on copper by CVD [19, 20]. Additionally, it is possible that these residual graphene grains serve as ‘seed grains’ for the subsequent cycle of growth. It has been shown in literature that best quality CVD graphene on copper is obtained by ‘pre-seeding’ graphene grains on the copper surface prior to graphene synthesis [21].

The principal advantage of the MAE process is that the copper foil is reusable indefinitely which should ultimately translate into decreased production of chemical waste. To illustrate this point, we made qualitative comparisons of the costs and environmental impacts of the MAE process to those of the conventional wet-etch method. The wholesale cost of copper on the global market is on the order of \$10 kg⁻¹ [22], but research quantities of copper foil are obtained for costs around 100 times higher [23]. The production energy of copper is 64 MJ kg⁻¹ [24], which translates to about 13 kg CO₂ emissions per kg of copper, using the current rate of generation in the US of 0.2 kg CO₂ MJ⁻¹ [25]. The MAE process can reuse the ~25 μm thick copper foil indefinitely, while the prevailing wet-etch method destroys it. While the MAE process does involve the etching of nickel (or cobalt), the MAE process etches two hundred times less metal than does the wet-etch method. We also expect that metallization

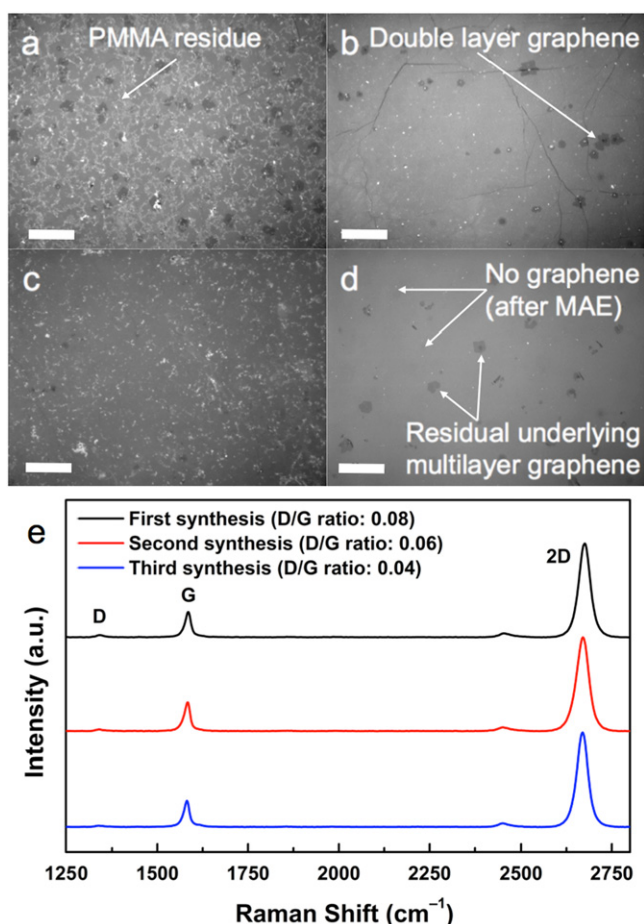


Figure 6. Optical micrographs of graphene transferred onto a Si/SiO₂ wafer from the same copper foil substrate after the first (a), second (b), and third (c) syntheses using the traditional wet-transfer method (scale bar 20 μm). Each consecutive synthesis after the transfer of graphene via nickel evaporation produced cleaner, better quality graphene. That is, the number of multilayer regions, which appear in the images as darker spots, decreased significantly from (a) to (c). We note that the white contamination visible in (a)–(c) is residual PMMA that could not be removed in the boiling acetone bath. Panel (d) represents the residual graphene grains (previously multilayer regions) on the copper substrate after exfoliation of graphene in the MAE process. (e) Raman spectra of the transferred graphene also indicated an improvement in quality upon consecutive synthesis of graphene on the same substrate (the D/G peak ratio decreased from 0.08 in the first growth to 0.04 in the third growth).

can be performed inexpensively (and with little waste) in a roll-to-roll manner as is done for metallized plastic foils for food packaging (e.g., potato chip bags) or under ambient conditions by electrodeposition. Moreover, the time it takes to etch the 150 nm nickel film completely is 3–5 s, whereas the time to etch the copper foil is at least 30 min. By avoiding the need for the preparation of the copper substrates after the first synthesis, the savings in time with the MAE process make it substantially more amenable to manufacturing than the conventional method. Additionally, while nickel and copper were etched with toxic FeCl₃ for convenience in the experiments described here, we expect that the FeCl₃ can be replaced with a more recyclable alternative such as ammonium persulfate (APS). Possible improvements in scalability include replacing

the thermal release tape, which is convenient for laboratory-scale experiments, by another adhesion control mechanism: electrostatic, magnetic, or kinetically controlled sticktion; for example with poly(dimethylsiloxane) (PDMS) stamps, which we have found can also exfoliate the graphene/nickel bilayer from the copper foil, and thus can probably redeposit the bilayer on a target substrate by kinetically controlled transfer printing.

4. Conclusion

We have developed a green, facile, and roll-to-roll compatible method for transferring large-area single-layer graphene to flexible substrates. With further improvements, the process has the capacity to produce films of similar quality to that of the prevailing method, which destroys an outsized amount of copper foil. Shortcomings in the current process include the anisotropic conductivity that is a consequence of manual peeling of the tape/nickel/graphene film from the copper substrate (step 3 in figure 1). This process has important implications for laboratory researchers, and for applications that demand very large areas of transparent electrodes or barrier films (e.g., solar farms based on organic or other thin-film technologies) due to the high production rates attainable with it through time, mass, and energy savings as well as reduced environmental impact and increased yield per batch. As compared to the traditional wet-etching process, MAE saves more than 60 min per batch (except the first run) by eliminating copper preparation steps (cleaning, electropolishing, annealing) and wet etching. Time required for Ni metallization and etching is negligible (seconds) considering that it is an industrial scale metallization process. Mass savings are due to the 188 times reduction in metal consumption (for 25 μm thick copper and 150 nm thick nickel) and energy savings are associated with removing the need to anneal foils for at least 30 min at more than 1000 °C prior to the synthesis of graphene. The 155 times reduction in the required corrosive waste handling represents a significantly lesser environmental impact. The yields per batch can be doubled in the MAE process due to harvesting graphene from both foil surfaces. Since the copper substrates are not etched in MAE, the robustness of the process can be significantly increased by using thicker, sturdier and more manageable copper foils (or plates) that will better withstand being repeatedly subjected to the high-temperature environment of the graphene synthesis chamber. We believe, furthermore, that a substantial decrease in the cost of large-area graphene will stimulate the development of applications that require very low cost—but high performance—graphene-enabled materials [26].

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Supporting information available

The online supporting information contains complete experimental protocols. This information is available free of charge via the Internet at pubs.acs.org.

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