

Application of Soxhlet Extractor for Ultra-clean Graphene Transfer

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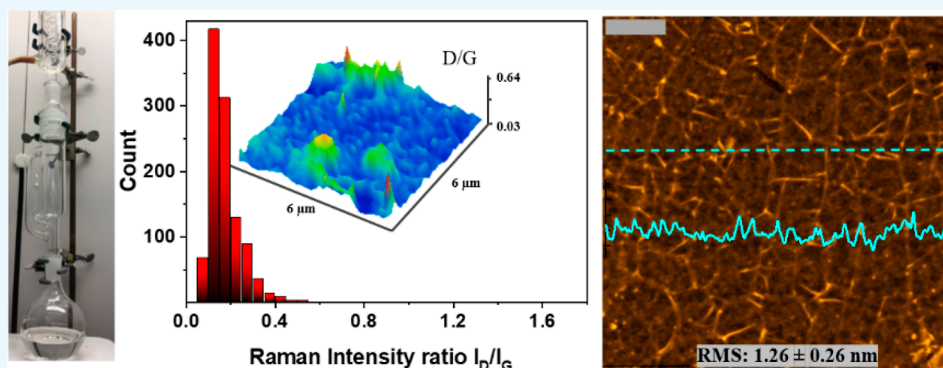
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ABSTRACT: Surface contamination experienced during polymer-assisted transfer is detrimental for optical and electrical properties of 2D materials. This contamination is usually due to incomplete polymer removal and also due to impurities present in organic solvents. Here, we report a simple, economical, and highly efficient approach for obtaining pristine graphene on a suitable substrate (e.g., SiO₂/Si) by utilizing Soxhlet extraction apparatus for delicate removal of the polymer with a freshly distilled ultrapure solvent (acetone) in a continuous fashion. Excellent structural and morphological qualities of the material thus produced were confirmed using optical microscopy, atomic force microscopy, scanning electron microscopy, and Raman spectroscopy. Compared to the conventional protocol, graphene produced by the current approach has a lower residual polymer content, leading to a root mean square roughness of only 1.26 nm. The amount of strain and doping was found to be similar, but the D-band, which is indicative of the defects, was less pronounced in the samples prepared by Soxhlet-assisted transfer. The new procedure is virtually effortless from the experimental point of view, utilizes much less solvent compared to the conventional washing procedure, and allows for easy scale-up. Extension of this process to other 2D materials would not only provide samples with superior intrinsic properties but also enhance their suitability for advanced technological applications.

INTRODUCTION

Graphene is one of the most important 2D materials due to its unique combination of properties such as high electron mobility,¹ high mechanical strength, and electrical and thermal conductivity.² Most importantly, advances in synthesis and scale-up have brought a positive outlook on commercialization of this promising material.³ After decades of research on graphene synthesis, chemical vapor deposition (CVD) has emerged as one of the best methods for controlled synthesis of high-quality monolayer and/or bilayer graphene.⁴ The procedure requires a suitable growth substrate (i.e., Cu or Ni), and the resulting graphene film is subsequently transferred onto a desired substrate such as SiO₂/Si,⁵ glass,⁶ paper,⁷ or flexible polymers.⁸

Different transfer procedures have been developed, but perhaps the most reliable technique available to date uses organic polymers (i.e., PMMA, PC, PVA, etc.) as the support layer.^{9–11} Due to the negligible thickness of graphene (ca. one atom), care needs to be taken during the transfer process to

prevent crack and wrinkle formation. Subsequently, avoiding transfer-induced damage is extremely challenging.^{12,13} Kang¹² et al. attributed some of the damage to incomplete removal of the sacrificial polymer (PMMA) from the graphene film due to high adhesion potential between the two substances. More so, impurities present in organic solvents (such as acetone, isopropyl alcohol, etc.) used during the transfer processes could lead to surface contamination with a resultant negative effect on carrier mobility in graphene.¹ This leads to an unfortunate scenario where repeated washing of the 2D material to achieve more complete removal of the polymer

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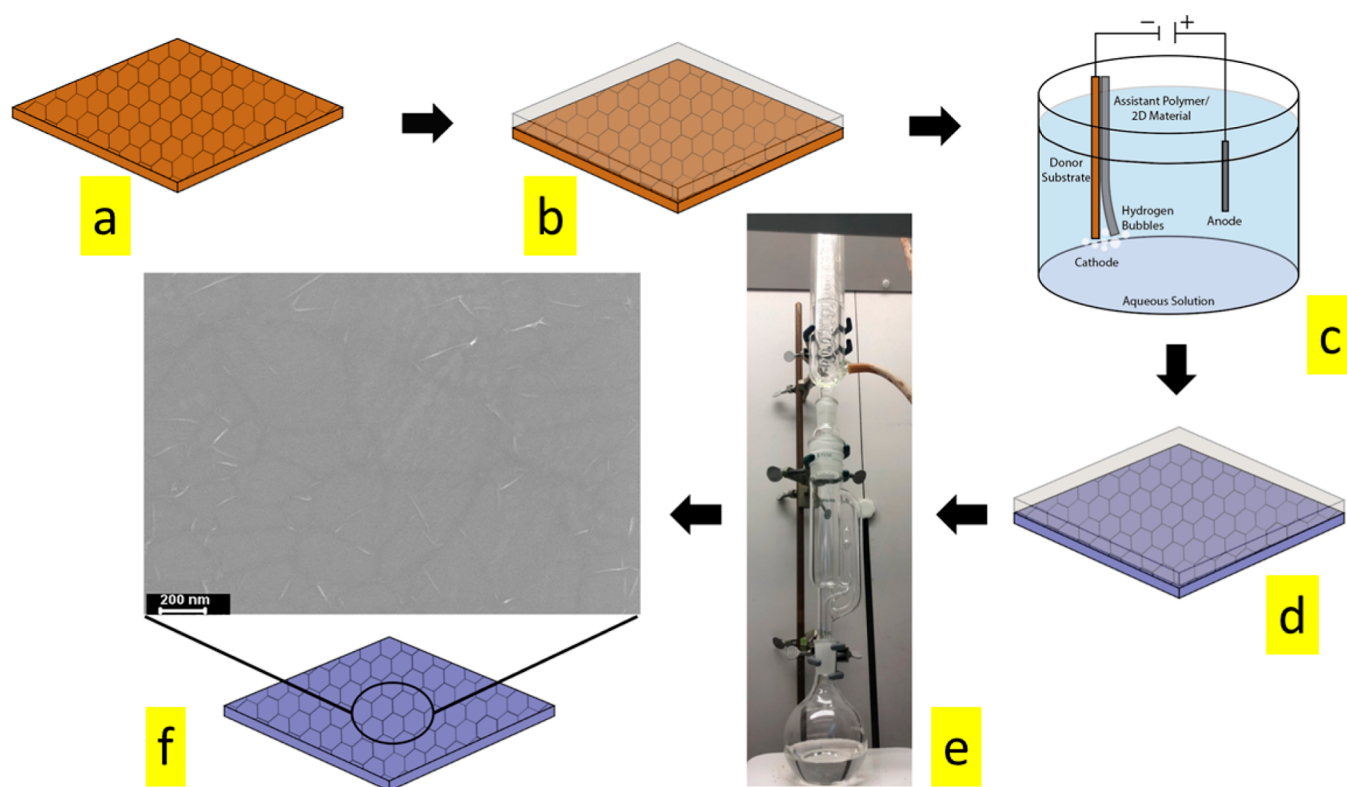


Figure 1. Schematic diagram of Soxhlet-assisted graphene transfer. (a) Graphene on Cu foil, (b) graphene spin-coated with PMMA, (c) Cu foil removal by the electrochemical method and subsequent transfer on the SiO₂/Si substrate, (d) graphene attached on the SiO₂/Si-PMMA composite, (e) Soxhlet apparatus setup for PMMA removal, and (f) ultra-clean graphene on the target substrate.

results in greater mechanical damage and contamination by the impurities present in the solvent.

Our experience supports the literature observations, suggesting that mechanical handling during polymer removal and solvent impurities are two key factors limiting the quality of transferred graphene. To address those limitations, we sought a simple experimental method that would minimize handling of the sample by the operator, while also providing a freshly distilled solvent for dissolving the polymer away. As explained below, both requirements are satisfied by removing the polymer in Soxhlet apparatus—a continuous (or, rather, an automated batch) solid–liquid extraction setup well known in organic, medicinal, and environmental chemistry.¹³ Soxhlet apparatus is indispensable in those cases where nearly complete extraction of a soluble material from the insoluble matrix is desired, for example, when extracting natural products from dilute sources. Another common application of the apparatus in synthetic chemistry is for separation of a poorly soluble product from insoluble byproducts—a particularly arduous task frequently encountered when working with polycyclic aromatic compounds.

RESULTS AND DISCUSSION

In the extraction procedure, the sample is placed into the Soxhlet extractor fitted with a reflux condenser and mounted on top of a flask containing the desired solvent. When the solvent in the bottom flask is heated to boiling temperature, the solvent vapor condenses in the reflux condenser at the top of the setup, filling the cup of the Soxhlet extractor containing the sample. Once the extractor cup fills up to the level of the siphon tube, the solvent automatically drains into the bottom

flask, carrying the soluble material with it. The solvent returning to the bottom flask vaporizes again, effectively concentrating the soluble material in the flask and producing a freshly distilled solvent portion for the next extraction cycle^{14–16} (Figure S1; also see the Supporting Information Video). This process is repeated in a continuous manner thus ensuring a complete extraction process. The technique has been used sparingly to either purify or wash polymers used as active layers in organic semiconductors,¹⁷ organic solar cells,¹⁸ or ultra-low dielectric thin films,¹⁹ and therefore, application of this technique to the graphene transfer process is of utmost interest. As a novel approach, we applied the Soxhlet extraction method for the removal of PMMA in graphene transfer and, as an extension, for rigorous purification of the as-transferred graphene. The post-transfer treatment using the Soxhlet technique has the following advantages: (1) simplicity, cost, and solvent recyclability; (2) minimization of material handling thus preventing mechanical damage; and (3) applicability of the protocol to a wide range of 2D materials and solvents and in photolithography. To assess the quality of the graphene transfer, we mapped the sample area by Raman spectroscopy and determined the surface roughness mostly stemming from polymer contamination by atomic force microscopy (AFM). Our transfer technique provides a simple approach for preparing cutting-edge quality large-scale graphene substrates for various applications by minimizing alteration to their intrinsic properties caused by incomplete polymer removal, excessive handling, and solvent contamination.

Graphene Transfer Procedure. The as-received CVD-grown graphene on Cu foil (provided by the 2DCC PSU or purchased from Sigma-Aldrich #773697) was initially spin-

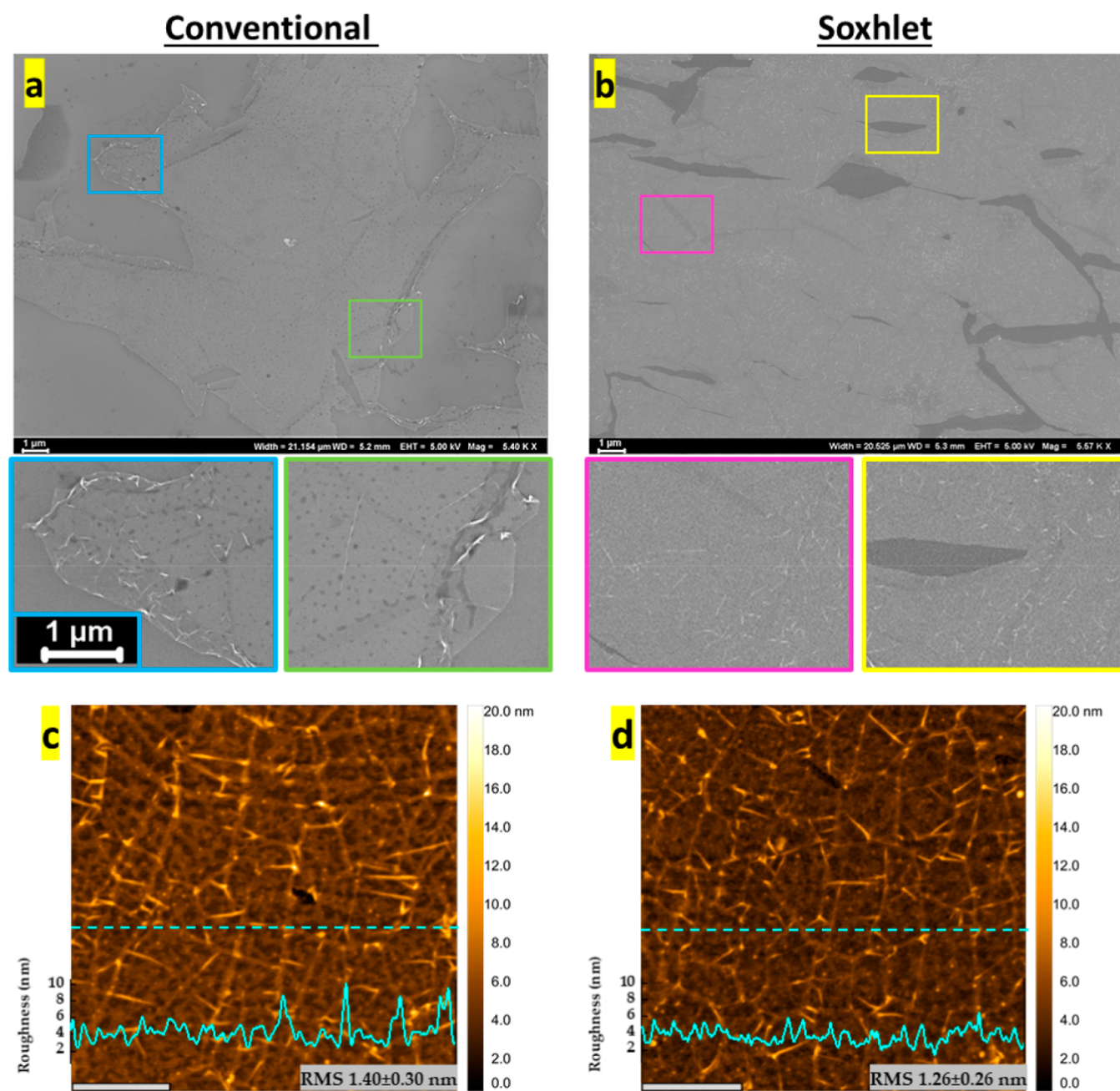


Figure 2. Characterization of transferred graphene films on SiO₂/Si substrates. SEM images of (a) conventional transfer method. (b) Soxhlet transfer method. Color framed insets represent zoomed areas. The AFM profile of (c) conventional transfer method. (d) Soxhlet transfer method, scale bare is 1 μm. Inset: The AFM line profile graph for both transfer techniques.

coated (Laurell EDC-650-8TFM) with 4 wt.% PMMA solution (ca. 950,000 g/mol; 99.9% purity) at 20,000 rpm for 5 min and thereafter thermally treated at 90 °C for 5 min and then at 150 °C for 2 h. The Cu layer underneath the coated graphene/PMMA composite was delaminated by the hydrogen bubbling method, leaving behind a PMMA sheet with attached graphene. The PMMA/graphene film was thoroughly rinsed with DI water for 10 min, and this step was repeated twice. Then, the polymer film/graphene floating in DI water was scooped onto a clean SiO₂/Si substrate. Subsequently, thermal treatments were performed to remove excess water trapped in between the SiO₂ substrate and PMMA/graphene film (at 95 °C for 10 min), and thereafter, the sample was baked at 135 °C for 30 min. The PMMA support was finally removed using

either Soxhlet apparatus or conventionally by dipping the substrate in reagent-grade acetone (Sigma-Aldrich, U.S.A; 99.9%) at 25 °C for 2 h.

Soxhlet Operations. The sacrificial PMMA polymer support was removed from the PMMA/graphene/SiO₂ composite via the newly developed Soxhlet extraction method. The apparatus, as shown in Figure 1, consists of a glass chamber equipped with a siphoning tube, vapor tube, and reflux condenser. The composite sample was carefully inserted into the extraction chamber using tweezers, and reagent-grade acetone was added into the flat bottom flask placed inside a heating mantle. The solvent was heated to achieve steady boiling of the solvent (>~57 °C), allowing ultra-pure acetone to evaporate and subsequently condense and fill up the

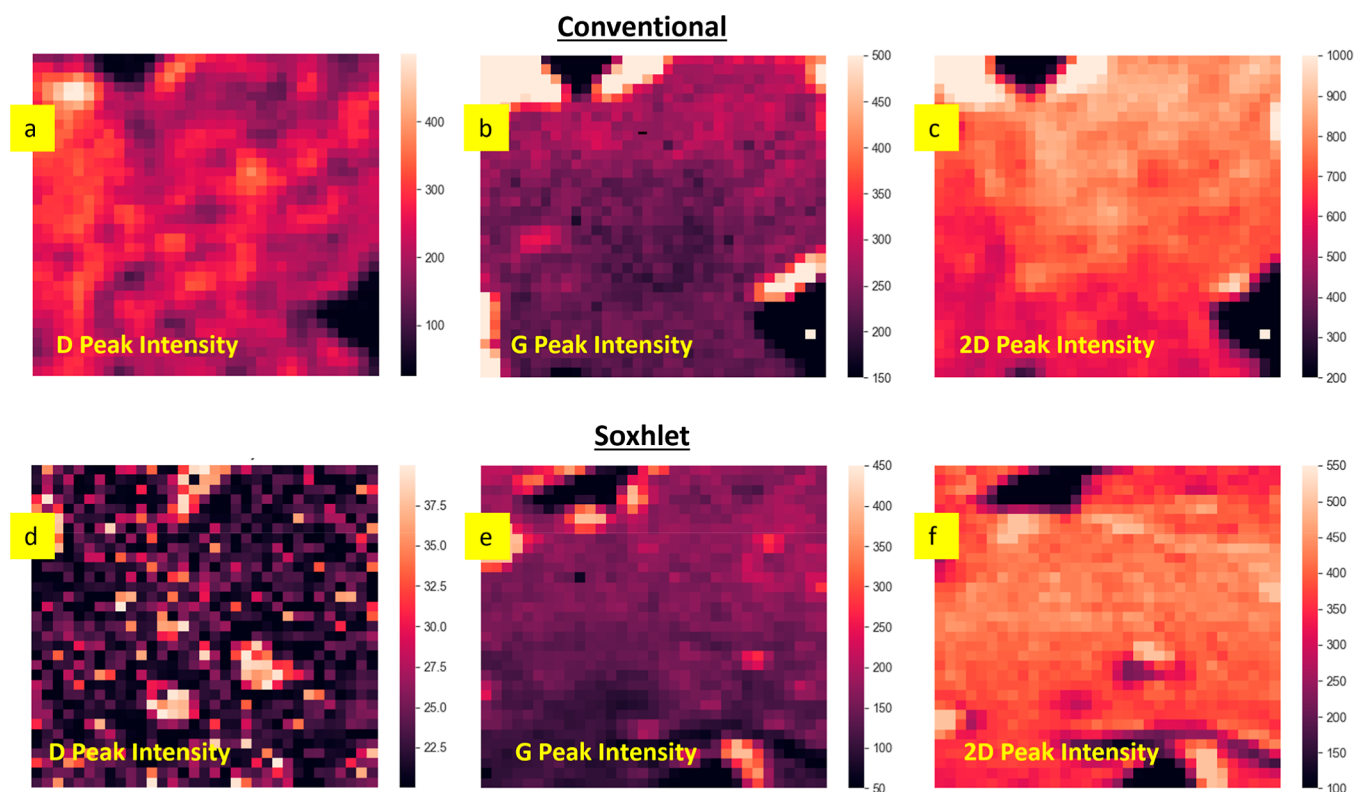


Figure 3. Corresponding maps of plotted results of Raman characterization ($10 \times 10 \mu\text{m}^2$) of graphene transferred with (a–c) conventional PMMA method and (d–f) Soxhlet-assisted PMMA method.

chamber containing the PMMA/graphene/ SiO_2 composite. The automated batch extraction process was allowed to continue for 4 h without any mechanical disturbance, after which the 2D material was removed from thimble, dried in a stream of N_2 gas, and then stored in an air-tight sample holder. For comparison purposes, a conventional purification/annealing process²⁰ was also carried out. Typically, the substrate containing the PMMA/graphene scaffold was thermally annealed to enhance the adherence of the scaffold onto the SiO_2 substrate and then placed in acetone at room temperature for 2 h to remove the PMMA layer. The substrate was then rinsed with isopropyl alcohol (HPLC grade; Sigma-Aldrich, U.S.A.; 99.9%) and dried with N_2 gas (99.99% purity).

Characterization. Raman spectra and point-by-point mapping were obtained with a HORIBA XploRa Raman Confocal system with an objective of 100X. The laser excitation wavelength was 532 nm, and a 1200 L mm^{-1} diffraction grating was used. A total of 2000 data points were collected on the transferred samples. The morphologies were analyzed using scanning electron microscopy (Zeiss Auriga FIB/FESEM) with an acceleration voltage of 5 kV and a working distance of 5 mm. AFM measurements were performed with an Oxford Research AFM (MFP-3D infinity) instrument using the tapping mode under ambient conditions, and Si tips coated with Al (TAP300AL-G probe, Budget Sensors) were used.

Soxhlet-Assisted Transfer onto Target Substrate. Our approach involves the use of Soxhlet apparatus as the key tool for benign PMMA removal in the graphene transfer process, including in situ preparation of ultra-pure acetone for dissolving the polymer (see the Supporting Information Video). In most transfer procedures, the polymer-removal

step is carried out by mechanically agitating the sample in a solvent directly received from a commercial supplier, which subjects the sample to excessive handling, impurities inevitably present in the solvent, and dust from the atmosphere. Therefore, contaminants in the solvent sometimes leave residues in addition to those resulting from incomplete PMMA removal (see SEM images in Figure 2a,b). The Soxhlet provides a quick solution to all the above-mentioned problems. Thus, the polymer removal is performed in an enclosed chamber, minimizing exposure to dust. Mechanical agitation of the sample is negligible, with solvent condensing around the sample in a very gentle fashion. The solvent is continuously purified by distillation during the process, without the need for a separate distillation setup, and minimizing solvent consumption. Most importantly, repeated washing of the sample with the freshly distilled solvent allows for essentially complete removal of the polymer from the graphene surface. Other advantages offered by our Soxhlet-assisted polymer-removal procedure include eliminating the need for a clean room to carry out pristine transfer processes and repeated recycling of the same batch of the solvent in a green “closed loop” setup.

Characterization of Graphene Transferred by both Techniques. The quality of the transfer was initially confirmed using optical microscopy (see Supporting Information Figure S1). A quick surface scan of graphene films obtained by both Soxhlet-assisted and conventional transfer techniques showed substantial coverage of the substrate by graphene. Intermittent cracks attributed to the damaging effect of PMMA during removal^{21,22} were observed with both techniques but appeared less pronounced in the Soxhlet-assisted method. It was also observed that the rough surface of

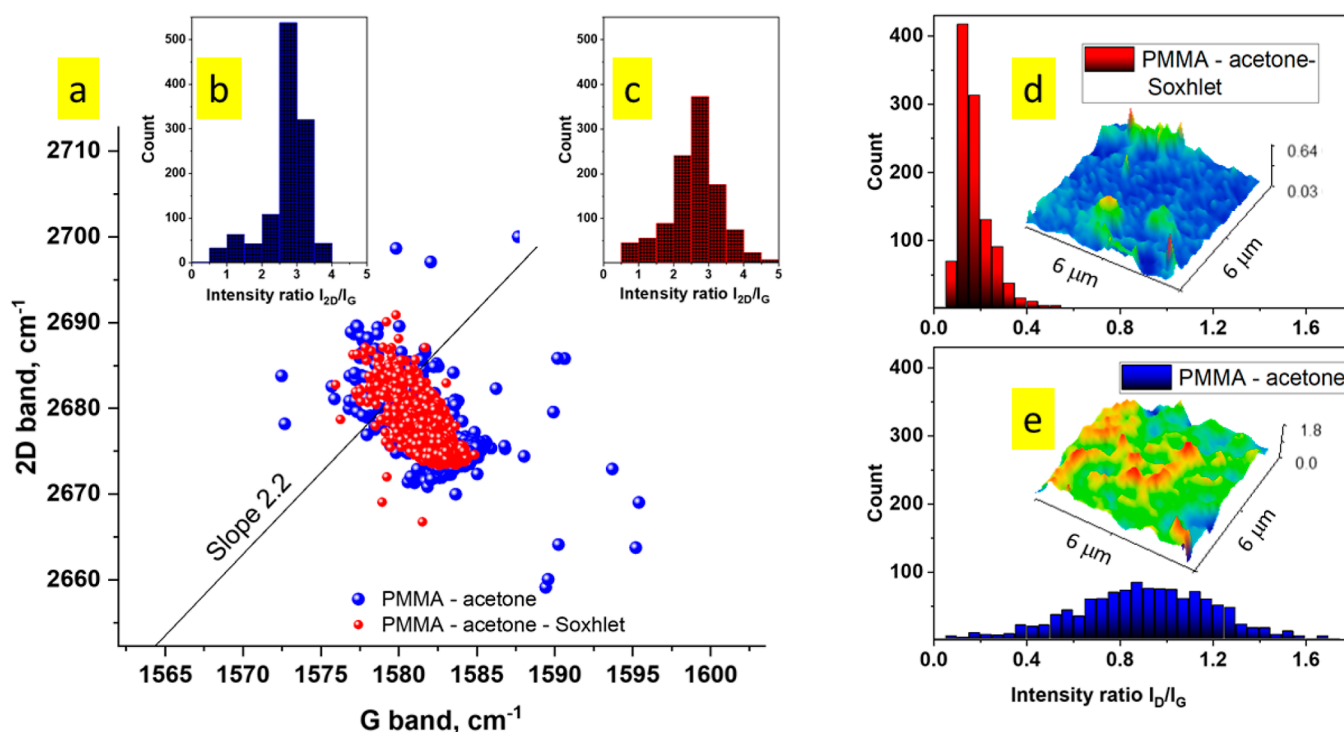


Figure 4. (a) Correlation map of the Raman G and 2D peak positions of graphene transferred with the conventional PMMA technique (blue) and Soxhlet-assisted PMMA technique (red). (b,c) Histogram of the 2D/G ratio with the same color code indicating the sample quality in general. (d,e) Histogram of the D/G ratio with the same color code as a signature of the defect amount. Insets show lateral distribution of the D/G ratio.

the Cu growth substrate left a distinctive pattern on the final graphene sheet transferred onto SiO₂/Si. The as-transferred graphene was subsequently analyzed by SEM (Figure 2a,b and insets), providing additional information at the nanoscale level.

Impurities introduced by acetone are clearly seen as dark dots in magnified areas of Figure 2a (conventional) but not in Figure 2b (Soxhlet). Residual PMMA contamination is evidenced by the presence of charged features in the SEM images, particularly only around the edges of the graphene sheet, and is more pronounced with the conventional protocol, thus suggesting less efficient polymer removal compared to the Soxhlet procedure. Furthermore, the presence of PMMA oligomer residues tends to mask the distribution of grain boundary defects induced during CVD growth on Cu, as seen in Figure 2a. In contrast, the surface morphology of graphene obtained by the Soxhlet method clearly revealed the grain boundary defects, apparently due to more effective PMMA removal by this novel approach (Figure 2b). More so, minimal mechanical damage was detected with the Soxhlet method, which is in contrast with the conventional immersion washing approach where significant folding and cracking were observed in the final graphene film.

We further assessed the surface topology of the graphene films transferred with both techniques using AFM (Figure 2c,d). Imaging graphene areas of about 4 × 4 μm², we observed less polymer contamination on the graphene film obtained by the Soxhlet method, as evidenced by the AFM line profile and the lower surface roughness root mean square value. We hypothesize that the improved efficiency of the PMMA removal in the Soxhlet-assisted transfer stems from nearly continuous contact of the PMMA–graphene/SiO₂ substrate with freshly distilled acetone, effectively disrupting well-known strong interactions between PMMA and graphene.^{1,23,24} Additional evidence for the importance of a gentle

yet rigorous polymer-removal procedure was obtained by micro-Raman spectroscopy, which was used to characterize graphene samples transferred either by Soxhlet or conventional methods (Figure 3a–f, also see Supporting Information Figure 2). Raman spectroscopy is a reliable technique to probe structural and electronic properties of graphene. An initial large-area scan in either the X- or Y-direction revealed a significantly greater number of defects/imperfections in graphene transferred by the conventional method. In contrast, the D-band was almost non-existent in the spectra of samples transferred using our Soxhlet method (see Supporting Information Figure S3). Defects in graphene originate either during the CVD growth²⁵ or transfer¹ processes, but it is noteworthy that both transfer processes were handled strictly identically prior to the PMMA-removal step, indicating that our novel transfer approach introduces fewer perturbations into the graphene film, leading to improved electronic and optical properties. Raman spectroscopy data are commonly used to evaluate the degree of doping and strain in graphene samples.^{26,27} Raman maps showed consistent results (Figure 3) for both techniques: the G and 2D bands of graphene appeared to be strong and homogeneous with the 2D peak full width half maximum of 32.4 cm⁻¹ over the whole area of characterization (see Supporting Information Figure S4) and typical 2D/G intensity ratios for monolayer graphene (Figure 4b,c, Supporting Information Figure S5). The amount of introduced strain and doping is very similar for both techniques, as can be seen from the correlation plot on Figure 4a. In contrast, one might observe that the D-band peak is more pronounced in samples prepared by the conventional graphene transfer method, which is evidenced by the calculated D/G ratios plotted in Figure 4d,e and Supporting Information Figure S5. Here, the graphene film obtained by the Soxhlet method features a very weak D band, with the average D/G intensity

ratio of only 0.17 ± 0.07 (Figure 4d). This indicates that the amount of defects introduced by the transfer technique is negligible. In contrast, the average D/G intensity ratio for the sample transferred using the conventional protocol is 0.90 ± 0.30 (Figure 4e), clearly indicating the presence of defects.

Repeated application of the proposed approach demonstrated high reproducibility, with expected minor sample to sample variations observed during the structural characterization (see Supporting Information Figure S2). The Soxhlet-assisted protocol has become the method of choice in our laboratory, allowing for multiple transfers to be conducted simultaneously, saving time and reagents, while preserving the quality and unique properties of graphene. A slight downside of our process is its energy intensive nature, and this is compensated by the conservation of the organic solvent (acetone) used in process purification and thus improving the carbon efficiency “cradle-to-cradle” of our process. The ability to process multiple samples at a time would further enhance the techno-economic feasibility of the Soxhlet-assisted protocol.

In conclusion, our Soxhlet-assisted method enabled transfer of a graphene film onto a target substrate with minimal surface contamination and damage associated with the conventional transfer process. The graphene film transferred by our new method shows fewer defects, as indicated by a substantially lower average D/G intensity ratio compared to the sample obtained by the conventional method. Although the amount of strain and doping appears similar in both techniques, less structural damage and more extensive polymer removal in the Soxhlet method could deliver materials of superior electrical, optical, and mechanical properties. Additionally, our new approach features experimental simplicity and reduced solvent use, potentially permitting the use of more affordable solvents of a lower degree of purification. Furthermore, this procedure can be applied for transfer of other delicate two-dimensional materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c07113>.

Additional details on data analysis, video file, supplementary figures, and references (PDF)

Soxhlet procedure (MP4)

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Author Contributions

Conceptualization, O.O.A., A.P., and T.I.; Experimental, O.O.A., S.P., A.T., and T.I.; Writing—original draft preparation, O.O.A., S.P., and T.I.; Writing—review and editing, O.O.A., A.P., and T.I. All authors have read and agreed to the published version of the article.

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Notes

The authors declare no competing financial interest.

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