An Economical and Scalable Method to Synthesize Graphitic-Like Films

Minh-Hai Tran, Ian Booth, Bruno G. daFonseca, Peter Berrang, Jeremy E. Wulff, and Alexandre G. Brolo*

Cite This: ACS Omega 2022, 7, 43548−43558

ABSTRACT: An economical and facile method to synthesize a precursor for carbon films and materials has been developed. This precursor can be easily coated onto substrates without binder reagents and then converted into a graphitic-like structure after mild thermal treatment. This approach potentially allows the coating of glass surfaces of different shapes and forms, such as the inside of a glass tube, for instance. The precursor consists of tetrahedral halocarbyne units which randomly combine through single electron transfer with organometallic compounds to create a poly(carbyne)-like polymeric material. Advanced characterization tools reveal that the synthesized product (poly(halocarbyne) or PXC, where X indicate the presence of halogens, is composed mostly of carbon, hydrogen, and a variable percentage of residual halocarbon groups. Therefore, it possesses good solubility in organic solvents and can be coated on any complex substrate. The coated PXC material produced here was annealed under mild conditions, leading to the production of a graphitic-like film on a glass substrate. The chemical homogeneity of the carbon material of the film was confirmed by Raman spectroscopy.

1. INTRODUCTION

In recent years, there has been a proliferation of research into the fabrication of graphene and graphene derivatives, driven by their interesting electrical and physical properties.1−5 Graphene-based materials can be used in a wide variety of fundamental and applied technologies, including electrocatalysis, electronics, and energy storage devices.6−11 There is also an increased interest in the utilization of graphene and graphite oxide in the biomedical field. For instance, there are several reports of their utilization in platforms for biosensing and drug delivery. The biocompatible and nontoxic properties of carbon are explored for antibody immobilization, and the π−π stacking structure enables high loading of hydrophobic drugs.12,13 Graphene oxide and related materials have large specific surface area with abundant functional groups, making them an ideal support for enzyme immobilization.14 However, despite all of these favorable properties and proven applications, the practical wide implementation of graphene-based devices and technologies faces the limitations of material cost, quality, and yield.15 In particular, common fabrication procedures, such as chemical vapor deposition, bottom-up synthesis, and synthesis on SiC are expensive, while low-cost alternatives, including liquid phase exfoliation and reduction of graphene oxide, have drawbacks in terms of yield and purity.15 Furthermore, the synthesis of graphene oxide, a widely used precursor for the graphene materials required for biomedical applications, involves the use of toxic, strong oxidizing reagent mixtures and produces uncontrollable undesirable functional groups.16,17 The low solubility and dispersion in organic solvents also hinders practical coating applications not only for graphene oxide but for all types of graphene-like materials.18−20

Here a new approach to the fabrication of graphitic-like compounds and coatings from a polymer precursor is introduced. This new approach should allow the coating of not only flat glass substrates but also glass surfaces of different shapes, such as tubular structures. Polycarbyne-family polymers, such as polyhydridocarbyne and polyphenylcarbyne, have a continuous random backbone network composed of a tetrahedral structure of sp3 carbon atoms. The polymerization is assumed to proceed by the coupling of free carbyne radicals generated by single-electron transfer.21,22 This polymer group is easily soluble in organic solvents and readily applied to
various substrates to form a film over large areas. This class of polymers has been proposed as a precursor for diamond-like carbon coatings, a material with excellent mechanical and tribological properties associated with sp3 $\mathrm{C}$–$\mathrm{C}$ bonding. Additionally, diamond-like carbon is inert, impervious, and biocompatible. In fact, diamond-like carbon materials, synthesized by chemical vapor deposition, have been used in biomedical applications. Currently, several of the reported methods to synthesize polycarbene polymers are based on dehalogenation of organic halogen to create carbyne units. The methods include the use of NaK alloy, sodium naphthalide, or electrolysis. These methods reportedly completely removed the halogen atoms and produced an sp3 network. Unlike these previous approaches, this work employs a synthetic route through an organomagnesium halide precursor. The main polymeric product is heterocarbyne units, exhibiting a structure combining sp3 and sp2 carbons, as well as ring structures. The polymer was soluble and processable, allowing it to be coated in different substrates and then thermally transformed into graphene-like materials. The chemical composition and quality of the coatings were evaluated by Raman mapping measurements.

2. EXPERIMENTAL SECTION

2.1. Materials. Bromoform (CHBr3, 99%), FeCl3 (anhydrous), and Mg (turnings, 99.5%) were purchased from MilliporeSigma and used as received. Tetrahydrofuran (THF, anhydrous) was bought from Merck and purified over sodium metal under argon. Pure powder graphite (natural, flask powder, 99%, Aldrich) was used as the reference for Raman spectroscopy.

2.2. Synthesis of Poly(halocarbene). Mg (2.0 g), FeCl3 (0.02 g), and 100 mL of THF were placed in a 500 mL three-neck round-bottom flask which was set up with a reflux condenser under argon gas. Bromoform was added in an initial 1 mL increment, until the reaction mixture turned brown and started to boil, as shown in Figure 1a. After waiting for the boiling behavior to slow down, a further 4 mL of bromoform was added gradually. The reactants were allowed to settle for 3 h, then worked up with dilute acid (5% HCl) and deionized water. The mixture exhibited two phases, with the polymer dissolved in THF existing as a top layer (Figure 1a) and an aqueous bottom layer that includes dissolved magnesium salt. A separatory funnel was used to collect the dissolved polymer, which was further extracted using a rotary evaporator. Figure 1 presents a series of photos to help visualize the synthetic steps. After drying under room temperature conditions overnight, around 0.5–1 g of a hard brown material was collected and then crushed with a mortar. The product, named poly-(halocarbyne) (PXC, where X represent the halogen in the compound), was insoluble in water, but it could be redissolved in THF to coat different types of surfaces/substrates. Dried hard-brown pieces of the final dried sample, named PXC polymer, then was treated by baking at 300 °C (10 °C/min ramp rate) under argon for 3 h, leading to a material named PXC-T polymer. This material presented a black shiny color like graphite (see Figure 1b).

2.3. Film Coating with PXC. Glass substrates were cleaned with methanol, THF, and dried in an oven overnight before the coating process. The synthesized PXC was dissolved in THF with a ratio of 1 mg/mL then spin coated with a speed of 500 rpm, leading to an estimated film thickness between 50 and 100 μm. Additionally, samples with graphite mixed with one to two drops of PXC solution to act as a binding reagent were also prepared and coated in the same way. The coated samples, pure polymer PXC and graphite mixed with PXC (G-PXC), were treated in an oven at 300 °C (10 °C/min ramp rate) under argon for 3 h. The resulting films are shown in Figure 1c, indicating visually a good coating quality of carbon materials obtained from PXC.

2.4. Characterization. The infrared spectra of the solid polymer samples were recorded on a total internal reflection Fourier-transformed infrared (TIR-FTIR) spectrometer (Per-
kinElmer Spectrum Two). The spectral region probed was from 500 to 4000 cm$^{-1}$ at a resolution of 2 cm$^{-1}$.

The polymer characteristics were measured by gel permeation chromatography/size exclusion chromatography (GPC/SEC) equipped with a Viscotek TDA 305 detector module with an integrated refractive index viscometer and light scattering detectors ($\lambda = 244.0$ nm) and with a column set of GMHxL. THF was used as the eluent at a flow rate of 1 mL/min, and the column temperature was set at 35 $^\circ$C. The polymer was analyzed at a concentration of 1 mg/mL after filtration through a 0.45 $\mu$m pore-size membrane prior to injection into the GPC columns. Monodisperse polystyrene standards were used for calibration. Polymer molecular weight distribution values were collected and analyzed using appropriate GPC software from Viscotek.

Surface morphology of the sample was observed by scanning electron microscopy (SEM, Hitachi S-4800, Japan) combined with an energy-dispersive X-ray (EDX) detector from Bruker Quantax EDS system. The higher resolution image of the sample was obtained using the ultrahigh resolution scanning electron microscope (STEM, Hitachi SU9000, Japan). The sample was prepared by coating on glass for SEM and EDX while a drop of dilute polymer in THF on the Cu grid was used for the STEM method. For the EDX analysis, a high accelerating voltage of 20 kV was used in order to generate peaks of elements which could be present in the samples.

Proton nuclear magnetic resonance spectra ($^1$H NMR), carbon spectra ($^{13}$C NMR), Distortionless Enhancement by Polarization Transfer (DEPT-135), and 2D-NMR (HSQC) were recorded using a 500 MHz Bruker spectrometer at ambient temperature. Proton chemical shifts are expressed in parts per million (ppm, $\delta$ scale) downfield from tetramethyl silane.

Raman spectroscopy was carried out on Renishaw Raman microscope (Renishaw Inc., US) using 633 and 532 nm diode lasers (Renishaw) and a 50X objective lens (Leica Microsystems, Germany). The original Raman spectra of dried sample powders (before being used for coating) were measured with 633 nm excitation wavelength. The chemical composition and homogeneity of the film were investigated by Raman mapping. In the Raman mapping technique, the excitation laser rasters across a predeterminate area of the sample and spectra are acquired at several spatial points (pixels) during the scan. The Raman mapping parameters utilized here included scanned areas of 32.5 $\mu$m by 32.5 $\mu$m, 2.5 $\mu$m scan steps, and a 532 nm laser excitation. The laser power was 1.75 mW. Each spectrum in the maps was acquired using 5 s integrations and three accumulations. The individual spectra of the maps were fitted using a customized code in Matlab containing two Gaussians and a baseline correction algorithm for the spectral region between 1050 and 1800 cm$^{-1}$.

Raman spectroscopy is a powerful tool for the identification and characterization of different types of carbon materials. It has been suggested that the hydrogenation level in carbon products can be inferred by a quantitative estimation of the background fluorescence observed in the Raman spectrum. A
method was developed and validated in the literature,\ref{30,31} and it will be applied in this work. The hydrogen content (\(H\) [\%at]) was then estimated based on the slope of the linear baseline (\(m\)) divided by G-band intensity (\(I(G)\)), according to eq 1 below:\ref{30,31}

\[
H_{[\%at]} = 21.7 + 16.6 \log \left( \frac{m}{I(G) - [\mu m]} \right)
\]  

(1)

3. RESULTS AND DISCUSSIONS

Pictures of glass slides coated with different types of PXC films are presented in Figure 1c. The pictures in Figure 1c confirm the fabrication of good quality films both before and after annealing. The small bubbles on the coating surface (Figure 1c) are caused by the evaporation of the THF solvent. Figure 2 presents further analysis of the morphology and elemental composition of the films by scanning electron microscopy (SEM/STEM), including samples of PXC before and after annealing treatment.

A smooth coating of the PXC on glass is evident from the low resolution (200 \(\mu m\) scale) SEM pictures (insert in Figure 2a). The picture in Figure 2a was obtained at the edge of the film, in a place where the border between the film and the glass is easily discernible, to highlight the thickness of the PXC coating. The adhesion of the PXC film to the glass substrate was excellent. High magnification images of PXC, shown in Figure 2a, indicate that the coating exhibits a microporous structure. As the image resolution increased in Figure 2b (5 \(\mu m\) scale), a network of long tangled fibers with a radius of around 2.5 \(\mu m\) is revealed. Figure 2b implies that the polymer (PXC) has a tangled “brain-like” structure. XRD characterization did not reveal any crystalline peak for PXC material, due to the amorphous nature of the polymer (as suggested in Figure 2a). A broad peak at \(\sim 26^\circ\) was presented after annealing (PXC-T), confirming graphitization.

The EDX results, shown in Figure 2c,d, reveal the changes in elemental composition in the polymer before and after thermal treatment. The EDX measurements were obtained five times from random spots on each coating. The composition variation determined by EDX was about 20\%. The synthesized PXC had a significant amount of bromine, but the halogen was readily eliminated by the thermal treatment (Figure 2c,d).

Figure 3 illustrates the vibrational characteristics of the PXC polymer before and after annealing. The peaks at 2930 and 2850 \(cm^{-1}\) are related to C–H stretching bands. Vibrations in those regions are common for both cyclic and aliphatic saturated hydrocarbons.\ref{32} Organic bromine compounds absorb strongly at 570 and 680 \(cm^{-1}\) due to C=Br stretching vibrations.\ref{33} The presence of unsaturation can be inferred by the presence of typical C=C stretch bands in the region between 1630 and 1690 \(cm^{-1}\). The strength of those bands provides a hint of the degree of olefins or aromatic groups in the polymer.\ref{33} The other peaks in the mid-IR fingerprint zone can also be assigned to methylene or methyl groups vibrations. The peaks at 970 and 1154 \(cm^{-1}\) are due to the out-of-plane and in-plane CH vibrations, respectively.\ref{34} The peak at 1230 \(cm^{-1}\) is characteristic of CH wagging vibration adjacent to bromine groups (–CH\(_2\)Br).\ref{32,33} The other features at 1367 and 1432 \(cm^{-1}\) indicate deformation vibrations (bending, wagging, rocking, or twisting) of CH and CH\(_2\) groups.\ref{32,33} Overall, the FTIR spectrum in Figure 3 strongly suggests that the polymer material (PXC) contains an abundance of hydrogen functional groups, as well as some other groups, such as bromine and olefins. The annealed sample, on the other hand, contains only broad peaks at about 1300–1400 \(cm^{-1}\) and at 1570 \(cm^{-1}\). The broad peaks in the range of 1300–1400 \(cm^{-1}\) are due to the residual randomly distributed C–H vibrations\ref{33} that are present after the dehalogenation process, while the broad feature at 1570 \(cm^{-1}\) is due to aromatic carbons\ref{33} formed after the thermal treatment. That result indicates that most functional groups, including hydrogen species, were eliminated by the thermal treatment.

Figure 4 presents 1D and 2D NMR results that provide further insights into the PXC polymer structure. Assignment of the NMR shifts was performed according to standard reference texts\ref{34,35} together with a comparison to representative small molecules, for which robust assignments are well-known. \(^1\)H–\(^1\)\(^3\)C correlations, made through the use of heteronuclear single quantum coherence experiments (HSQC; Figure 4d), were particularly valuable in establishing the structure of various groups within the polymer material.

The chemical shifts in the \(^1\)H NMR spectrum shown in Figure 4a can be categorized into several discrete ranges. Starting at the upfield end of the spectrum, we observed well-resolved signals at ca. 0.9 and 1.3 ppm. The 0.9 ppm signal correlated in the HSQC spectrum to at least three \(^1\)\(^3\)C signals, spanning from 14–23 ppm. The most prominent of these \(^1\)\(^3\)C signals (at 21.2 ppm) displayed a positive projection in the DEPT-135 spectrum (Figure 2c). As a result, the 0.9 ppm \(^1\)H resonance can be confidently assigned to methyl groups present on the polymer chain. Similarly, the 1.3 ppm signal correlated in the HSQC spectrum to a grouping of \(^1\)\(^3\)C signals between 24 and 38 ppm, with the most prominent signal in this range (at 29.7 ppm) displaying a negative projection in the DEPT NMR. Taking these data into account, the 1.3 ppm \(^1\)H resonance can be assigned to methylene groups within the polymer.

Interestingly, the most intense signal in the upfield region of the \(^1\)H NMR spectrum is a large singlet at 1.44 ppm, which correlates to \(^1\)\(^3\)C signals appearing between ca. 20 and 38 ppm. These are approximately the chemical shifts at which one would expect aliphatic methylene groups to come into resonance, and in keeping with this hypothesis we found that the most prominent of the associated \(^1\)\(^3\)C signals (at 30.3 ppm) displayed a positive projection in the DEPT spectrum. Collectively, these data strongly argue for the assignment of
Figure 4. continued
the 1.44 ppm $^1$H resonance to methyne groups within the PXC polymer.

Moving further downfield, a strong singlet at 2.28 ppm can be observed, which corresponds to a $^{13}$C resonance at ca. 21 ppm. This pattern of signals clearly indicates the presence of allylic (and/or benzylic) CH groups present within the molecule. Further evidence for allylic groups comes from the observation of signals corresponding to olefinic protons (ca. 5 ppm) and carbons (104–130 ppm). Somewhat surprisingly, given the simple alkyl halide starting material, we also saw clear evidence of aromatic groups, indicated by signals in the $^1$H NMR between 6.4 and 7.4 ppm, and in the $^{13}$C NMR between 125 and 152 ppm. The most downfield of these signals do not appear in the DEPT-135 spectrum (or the HSQC), indicating the presence of quaternary aromatic carbon atoms.

Critically, additional cross-peaks can be observed in the HSQC spectrum in the range between 3.1 and 3.9 ppm in the $^1$H channel, and 34–68 ppm in the $^{13}$C channel. These ranges correspond to the window for alkyl bromide species, and so (together with EDX data presented above indicating the presence of bromide) the signals are assigned as corresponding to alkyl bromide motifs within the polymer chain.

Based upon the characterization results presented in Figures 2–4, a plausible mechanism for PXC polymerization is presented in Figure 5. The process begins by single-electron transfer from the metallic magnesium to the organohalide substrate, consistent with the mechanism for Grignard activation. From here, either an organomagnesium halide can be produced (i.e., a Grignard reagent, which functions as a synthetic equivalent to a carbanion) or a carbon radical. Either of these energetic species can undergo couplings with themselves (e.g., through radical–radical couplings) or with a second equivalent of the organohalide starting material (e.g., through $S_N1$, $S_N2$, or $S_{RN1}$ addition) to produce a new C–C bond. Overall, bond formation is achieved through the loss of one equivalent of Br$_2$.

The process can then be repeated several times over, to produce a mixture of linear polymers and cyclic species, each of which has the formula (CHBr)$_n$. While a variety of ring sizes would be expected for cyclic products, six-membered rings will usually predominate given their lower intrinsic strain energy. Of course, each of these (CHBr)$_n$ intermediates can undergo further activation by magnesium, leading to cross-linking of polymer chains, and coupling of cyclic species either with other rings or with the growing polymers.

Alkene and aryl groups in the polymer structure likely emerge through a combination of elimination pathways. E1 and E2 eliminations will form a new C=C double bond through the loss of HBr, while activation of alkyl halides by Mg (to form an intermediate Grignard species) will lead to olefination through the loss of MgBr$_2$. Radical-mediated beta-scission pathways are also possible, while vinylogous eliminations (e.g., $S_N2'$) could lead to the formation of conjugated dienes. For hexacyclic organohalides, second and third eliminations (of either HBr or MgBr$_2$) will be faster than the initial elimination step, such that the likely product will be a substituted benzene ring. If E1 and E2 eliminations dominate the elimination cascade, then each aromatic ring would be expected to contain three protons arrayed in either a 1,3,6- or 1,3,5-relationship around the ring, with the latter distribution being statistically more likely.

Finally, methyl and methylene groups within the polymer can be explained by activation of organobromide groups with magnesium, followed by quenching of the resulting Grignard species by a proton donor such as water. This is likely to be a slower process than the Wurtz-type couplings that lead to chain extension and polymer cross-linking, however, which explains the relatively low abundance of CH$_3$ and CH$_2$ species, compared with CH species, observed in the $^1$H NMR spectrum.

The polymer molecule weight was determined by GPC. The number-average molecular weight ($M_n$) was 50,036 g/mol.
and the mass-average molecular weight \( (M_W) \) was 121 068 g/mol. Accordingly, the derived value of molecular weight polydispersity ratio \( (M_w/M_n) \) is 2.42 due to the branching or cross-linking structure of the polymer PXC, as described in Figure 5.

Raman spectroscopy is used extensively to characterize graphene and graphitic materials because of its sensitivity to \( \text{sp}^2/\text{sp}^3 \) ratios in carbon allotropes. Figure 6 shows the Raman spectra of powder samples of the PXC polymer before (PXC) and after thermal treatment (PXC-T), graphite (G), and the mixture of graphite/PXC after thermal treatment (G-PXC-T). The Raman spectrum of the PXC polymer (Figure 6a) does not present any discernible Raman peak, due to the amorphous nature of the branch polymer and the high level of hydrogenation, which leads to a strong luminescence background. The Raman spectrum of crystalline graphite, shown in Figure 6c, displays three typical peaks, assigned to the D, G, and 2D bands at 1328, 1569, and 2673 cm\(^{-1}\), respectively. These three peaks derive from different carbon hybridization structures. Specifically, the G-band is sensitive to stretching vibrations of \( \text{sp}^2 \)-hybridized carbon, while the D-band originates from either disordered graphene and relative to...
the sp³ site of aromatic structures.³ Combined with the G band, the 2D band is a Raman signature of graphitic sp² materials.³ The Raman spectrum of the thermally treated PXC material (PXC-T) in Figure 6b displays a graphite-like structure, demonstrated by the appearance of D and G peaks after thermal treatment. These peaks were deconvoluted in Figure 6b by using Voigt functions.³⁸ The dominant sp³ peak (G band) indicates a predominant formation of double bonds after thermal treatment (PXC-T). The mild thermal treatment performed on the PXC polymer removed the halogen groups (see EDX in Figure 2d) while the coating quality was conserved (Figure 1c).

On the other hand, Figure 6d shows that the thermal treatment of the sample containing graphite and PXC (G-PXC-T) presents a sharp peak at 1578 cm⁻¹ due to graphite, as well as the G and 2D peaks from the PXC (deconvoluted bands in Figure 6d). The background in Figure 6c and d indicates that some hydrogen remained in the annealed film. The quantification of the levels of hydrogen was explored by Raman mapping.

A challenge for the application of graphene-type materials in devices is related to the processability of the materials, particularly for the difficulties in producing good quality coatings on surfaces of arbitrary shape. Graphene films are routinely fabricated by complex routes, such as chemical vapor deposition (CVD) or functionalization methods.⁴⁰ As shown in Figure 1c, the PXC polymer reported here produces good quality coats on large area surfaces, which can be annealed to generate a graphitic film. The quality and chemical homogeneity of the film was determined by Raman mapping. Raman maps allow an evaluation of the spatial distribution of the film composition and help to further elucidate the sp³/sp² structure of both the thermally treated PXC (PXC-T) and the mixture of PXC/graphite (G-PXC-T) films. The Raman map results include a large number of spectra to provide a correlation between the spectroscopic response and the existence of specific chemical compounds at a certain position on the sample surface.⁴¹ 196 spectra were obtained from each film. Figure 7 shows the comparison of Raman parameter results obtained for two types of thermally annealed films, PXC-T and G-PXC-T. Specific spectroscopic parameters, including the Raman shift of the G peak (Pos(G)), full width at half-maximum of the G peak (fwhm(G)), ratio of intensities of D and G peaks (I(D)/I(G)), and hydrogen content (H%), estimated using eq 1, were extracted from each individual Raman spectrum in the maps and treated to generate histograms. It is important to point out that the Raman parameters provide information about the chemical characteristics of the film and their variation on the surface indicating changes in the composition of the graphitic material within a few micrometers. The sharp distribution of the position of the G band around 1585 cm⁻¹ (Pos(G)) of the PXC-T material (Figure 7a) demonstrates the ability of this material to form relatively homogeneous coatings. A sharp distribution is also observed at Figure 7b for the full-width at half-maximum of the G band (FHMW(G)) for the annealed samples. The ratio between the intensities of the D- and G-peaks are less than unity for both PXC-T and G-PXC-T samples in Figure 7c, indicating that the annealed PXC films are composed of carbon materials with a predominant sp² character. The EDX result in Figure 2 implied that oxygen and halogen functional groups leave the PXC material upon

Figure 6. Raman spectroscopy results. The excitation wavelength was 633 nm (a) PXC, (b) PXC after thermal treatment (PXC-T), (c) pure graphite (G), and (d) mixture of graphite/PXC after thermal treatment (G-PXC-T).
annealing. This result is confirmed by Raman, which presented a dominant signature of graphitic materials. On the other hand, the background luminescence in the Raman data of the PXC-T suggests the presence of residual hydrogenated structures, possibly aromatic or olefinic structures. The average hydrogen content percentage present in the PXC-T samples, calculated using eq 1, was about 30% (see histogram in Figure 7d). The G-PXC-T film seems to exhibit a broader spatial distribution for H[at%] than the PXC film (Figure 7d). The larger spatial variation in the amount of hydrogen seems to indicate that the graphitic starting material should have had an initial hydrogen load that functionalized the PXC upon annealing. The parameters for other spectroscopic characteristics of G-PXC-T, including Pos(G), fwhm(G), and I(D)/I(G) present slightly broader distributions than for the PXC-T films. This difference in homogeneity can be attributed to the dual composition of the starting material (graphite + polymer precursor), which probably led to a mixture of graphitic products after annealing. In any case, it is possible to conclude that films with reasonable chemical characteristics and spatial homogeneity can be generated using graphite as a binding agent.

4. CONCLUSION

The current approaches to generate films of graphene and graphitic materials possess some important drawbacks in terms of cost and complexity. Here, we introduced a pathway to the synthesis of graphitic-like materials through a polymerization method followed by annealing. The branched polymer structure (PXC) was mainly composed of carbon and hydrogen arranged as a mixture of aromatic and olefinic systems. The PXC polymer, either pure or mixed with another component, can be used to coat glasses and other surfaces of arbitrary shapes. This is achieved by simple processes, such as dip-coating and spin-coating of the THF-soluble polymer. These coats can be annealed to generate a film of graphitic materials. The graphitic films on glass surfaces were chemically uniform, as revealed by Raman mappings. The main advantage of this coating technique is that it allows the generation of good quality graphitic films on glass surfaces of complex shapes (not only planar structures), such as tubular structures. The approach presented here indicates a chemically processable route for the deposition of graphitic species that has the potential to be useful for device fabrication.

■ AUTHOR INFORMATION

Corresponding Author
Alexandre G. Brolo — Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada; Center for Advanced Materials and Related Technologies, University of Victoria, Victoria, British Columbia V8W 2Y2, Canada; orcid.org/0000-0002-3162-0881; Email: agbrolo@uvic.ca

Authors
Minh-Hai Tran — Department of Chemistry, University of Victoria, Victoria, British Columbia V8W 3V6, Canada; Center for Advanced Materials and Related Technologies, University of Victoria, Victoria, British Columbia V8W 2Y2, Canada; orcid.org/0000-0003-4658-4956

Figure 7. Histograms of Raman mapping of baked PXC film (PXC-T) and graphite mixed with PXC (G-PXT-T) film with (a) the Raman shift of the G peak, (b) full width at half-maximum of the G peak, (c) ratio of intensities of D and G peaks, and (d) hydrogen content.
The authors declare no competing financial interest.

Notes

The authors thank CFIs, BCKDF, and the University of Victoria for equipment grants.

**ACKNOWLEDGMENTS**

This work was funded by the MITACs Accelerate Program. The authors thank CFIs, BCKDF, and the University of Victoria for equipment grants.

**REFERENCES**

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. Two-dimensional gas of massless Dirac fermions in graphene. Nature 2005, 438, 197–200.

(2) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. Experimental observation of the quantum Hall effect and Berry’s phase in graphene. Nature 2005, 438 (7065), 201–204.

(3) Ferrari, A. C. Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. Solid State Commun. 2007, 143 (1–2), 47–57.

(4) Bunch, J. S.; van der Zande, A. M.; Verbridge, S. S.; Frank, I. W.; Tanenbaum, D. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Electromechanical Resonators from Graphene Sheets. Science 2007, 315 (5811), 490–493.

(5) Lee, C.; Wei, X.; Kysar, J. W.; Hone, J. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science 2008, 321 (5887), 385–388.

(6) Geim, A. K. Graphene: Status and Prospects. Science 2009, 324 (5934), 1530.

(7) Chen, D.; Tang, L.; Li, J. Graphene-based materials in electrochemistry. Chem. Soc. Rev. 2010, 39 (8), 3157–3180.

(8) Guo, S.; Dong, S. Graphene nanosheet: synthesis, molecular engineering, thin film, hybrids, and energy and analytical applications. Chem. Soc. Rev. 2011, 40 (5), 2644–2672.

(9) Brownson, D. A. C.; Kompouris, D. K.; Banks, C. E. An overview of graphene in energy production and storage applications. J. Power Sources 2011, 196 (11), 4873–4885.

(10) Lee, X. J.; Hiew, B. Y. Z.; Lai, K. C.; Lee, L. Y.; Gan, S.; Thangalazhy-Gopakumar, S.; Rigby, S. Review on graphene and its derivatives: Synthesis methods and potential industrial implementation. J. Taiwan Inst. Chem. Eng. 2019, 98, 163–180.

(11) Tsang, C. H. A.; Huang, H.; Xuan, J.; Wang, H.; Leung, D. Y. C. Graphene materials in green energy applications: Recent development and future perspective. Renewable Sustainable Energy Rev. 2020, 109656.

(12) Nurunnabi, M.; Parvez, K.; Nafijujman, M.; Reviri, V.; Khan, H. A.; Feng, X.; Lee, Y.-k. Bioapplication of graphene oxide derivatives: drug/gene delivery, imaging, polymeric modification, toxicology, therapeutics and challenges. RSC Adv. 2015, 5 (52), 42141–42161.

(13) Chung, C.; Kim, Y.-K.; Shin, D.; Ryooy, S.-R.; Hong, B. H.; Min, D.-H. Biomedical Applications of Graphene and Graphene Oxide. Acc. Chem. Res. 2013, 46 (10), 2211–2224.

(14) Zhang, J.; Zhang, F.; Yang, H.; Huang, X.; Liu, H.; Zhang, J.; Guo, S. Graphene Oxide as a Matrix for Enzyme Immobilization. Langmuir 2010, 26 (9), 6083–6085.

(15) Raccichini, R.; Varzi, A.; Passerini, S.; Scrosati, B. The role of graphene for electrochemical energy storage. Nat. Mater. 2015, 14 (3), 271–279.

(16) Shao, G.; Lu, Y.; Wu, F.; Yang, C.; Zeng, F.; Wu, Q. Graphene oxide: the mechanisms of oxidation and exfoliation. J. Mater. Sci. 2012, 47 (10), 4400–4409.

(17) Chen, C.-H.; Hu, S.; Shih, J.-F.; Yang, C.-Y.; Luo, Y.-W.; Jhang, R.-H.; Chiang, C.-M.; Hung, Y., Jr. Effective Synthesis of Highly Oxidized Graphene Oxide That Enables Wafer-scale Nanopatterning: Preformed Acidic Oxidizing Medium Approach. Sci. Rep. 2017, 7 (1), 3908.

(18) Konios, D.; Stylianakis, M. M.; Stratakis, E.; Kymakis, E. Dispersion behaviour of graphene oxide and reduced graphene oxide. J. Colloid Interface Sci. 2014, 430, 108–112.

(19) Neldyudov, V. V.; Khafizov, N. R.; Sedov, I. A.; Dimiev, A. M. New insights into the solubility of graphene oxide in water and alcohols. Phys. Chem. Chem. Phys. 2017, 19 (26), 17000–17008.

(20) Xu, C.; Wu, X.; Zhu, J.; Wang, X. Synthesis of amphiphilic graphite oxide. Carbon 2008, 46 (2), 386–389.

(21) Bianconi, P. A.; Joray, S. J.; Aldrich, B. L.; Sumranjit, J.; Duffy, D. J.; Long, D. P.; Lazorick, J. L.; Raboin, L.; Kearns, J. K.; Smulligan, S. L.; Babyak, J. M. Diamond and Diamond-Like Carbon from a Preceramic Polymer. J. Am. Chem. Soc. 2004, 126 (10), 3191–3202.

(22) Rieke, R. D.; Chen, T.-A. Facile Synthesis of Polyphenylcarbyne): A Precursor for Diamondlike Carbon. Chem. Mater. 1994, 6 (5), 576–577.

(23) Huang, S. M.; Sun, Z.; An, C. W.; Lu, Y. F.; Hong, M. H. Electron field emission from polymer films treated by a pulsed ultraviolet laser. J. Appl. Phys. 2001, 90 (5), 2601–2605.

(24) Robertson, J. Diamond-like amorphous carbon. Mater. Sci. Eng., R 2002, 37 (4), 129–281.

(25) Anne Thomson, L.; Law, F. C.; Rushton, N.; Franks, J. Biocompatibility of diamond-like carbon coating. Biomaterials 1991, 12 (1), 37–40.

(26) Enomoto, K.; Hasebe, T.; Asakawa, R.; Kamijo, A.; Yoshimoto, Y.; Suzuki, T.; Takahashi, K.; Hotta, A. Controlling the drug release rate from biocompatible polymers with micro-patterned diamond-like carbon (DLC) coating. Diamond Relat. Mater. 2010, 19 (7–9), 806–813.

(27) Schroeder, A.; Franck, G.; Brunink, A.; Hauert, R.; Mayer, J.; Wintermantel, E. Titanium containing amorphous hydrogenated carbon films (a-C:H/Ti): surface analysis and evaluation of cellular reactions using bone marrow cell cultures in vitro. Biomaterials 2000, 21 (5), 449–456.

(28) Bulychev, B. M.; Zvukova, T. M.; Sizov, A. I.; Aleksandrov, A. F.; Korobov, Y. A.; Kanzubya, M. V.; Khomich, A. V. Poly(naphthalenehydrocarbonyl): synthesis, characterization, and application to preparation of thin diamond films. Russ. Chem. Bull. 2010, 59 (9), 1724–1728.

(29) Nur, Y.; Cengiz, H. M.; Pitcher, M. W.; Toppare, L. K. Electrochemical polymerization of hexachloroethane to form poly(hydridocarbyne): a pre-ceramic polymer for diamond production. J. Mater. Sci. 2009, 44 (11), 2774–2779.

(30) Buijnsters, J. G.; Gago, R.; Jiménez, I.; Camero, M.; Agulló-Rueda, F.; Gómez-Aleixandre, C. Hydrogen quantification in diamond-like carbon films by infrared, Raman, and x-ray absorption near edge spectroscopies. J. Appl. Phys. 2009, 105 (9), 093510.

(31) Casiraghi, C.; Piazza, F.; Ferrari, A. C.; Grambole, D.; Robertson, J. Bonding in hydrogenated diamond-like carbon by Raman spectroscopy. Diamond Relat. Mater. 2005, 14 (3), 1098–1102.
(32) Larkin, P. Infrared and Raman Spectroscopy; Principles and Spectral Interpretation; Elsevier, 2011.
(33) Infrared Characteristic Group Frequencies: Tables and Charts, Second Edition (Socrates, George). J. Chem. Educ. 1995, 72 (4), A93.
(34) Jacobsen, N. E. NMR Data Interpretation Explained: Understanding 1D and 2D NMR Spectra of Organic Compounds and Natural Products; Wiley, 2017; p 656.
(35) Spectroscopic Methods in Organic Chemistry. In Spectroscopic Methods in Organic Chemistry; Georg Thieme Verlag, 2008.
(36) Grignard Reagents and Transition Metal Catalysts: Formation of C-C Bonds by Cross-Coupling; De Gruyter, 2016.
(37) Wiberg, K. B. The Concept of Strain in Organic Chemistry. Angew. Chem., Int. Ed. Engl. 1986, 25 (4), 312–322.
(38) Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. Lett. 2006, 97 (18), 187401.
(39) Wang, S.; Zhu, J.; Wang, J.; Yin, X.; Han, X. Raman spectroscopy and mechanical properties of multilayer tetrahedral amorphous carbon films. Thin Solid Films 2011, 519 (15), 4906–4909.
(40) Tong, Y.; Bohm, S.; Song, M. Graphene based materials and their composites as coatings. Austin J. Nanomed. Nanotechnol. 2014, 1 (1), 1003.
(41) Larsen, A. R. Raman Spectroscopy of Polymers; Applied Polymer Science: 21st Century, 2000; p 780.