Transmissible plasma-evolved suspended graphene near room temperature

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Article

Keywords: graphene production, suspended graphene, pulsed arc plasma, transmissible plasma-evolved graphene (TPEG)

Posted Date: October 13th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-88971/v1>

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Abstract

Top-down and bottom-up approaches are widely adopted to synthesize graphene from different carbon sources with the help of catalysts. The chemical vapour deposition (CVD) of carbon feedstock onto a catalyst surface, carbon species that are excited by a plasma, and high-energy laser irradiation of carbon surfaces are important methods for graphene production. However, for most techniques, high processing temperatures and time-consuming transfer and chemical treatment processes are essential to produce graphene for subsequent applications; therefore, a simple and straightforward alternative process is highly desirable. Here, we report a simple technique to produce suspended graphene with a short processing time and low temperature by employing a pulsed arc plasma. The catalytically active metal plasma is revealed to be transmissible through a suspended amorphous carbon (a-C) membrane, and the a-C evolves into highly graphitized C (sp^2 -C). The produced sp^2 -C is referred to as transmissible plasma-evolved graphene (TPEG). In this process, a pulsed arc plasma is generated from negatively biased metal electrodes, where each pulse lasts a fraction of a second, and the catalytic activity of the plasma is tuned by both the applied bias voltage and the number of pulses (not more than 10). Furthermore, TPEG with nanoparticles (NPs) and single-walled carbon nanotubes (SWCNTs) are successfully produced by employing a dual pulsed arc plasma source, indicating that TPEG could be utilized for the characterization of zero-dimensional (0D) and one-dimensional (1D) materials, such as graphene synthesized by CVD. It is very surprising that even a-C on a polymer support is successfully transformed into graphene by the TPEG technique without sacrificing the polymer support, which confirmed that TPEG is formed near room temperature.

Main Text

A thin membrane or a net held on a grid with a certain pitch has been widely used for the characterization of nanomaterials by transmission electron microscopy (TEM) (the suspended part of grid is referred to as a mesh hereafter in this paper). In particular, suspended graphene and other two-dimensional materials are eagerly utilized for novel two-dimensional materials characterization¹⁵⁻¹⁷, even though a complicated and time-consuming process needs to be followed for commercial graphene grid processing¹⁸. Furthermore, a suspended graphene array on an appropriate pitch support can be used as a harmonic oscillator and pressure sensor^{19,20}. In this study, we utilize amorphous carbon (a-C) membranes on TEM grids as a carbon source and plasma-excited metals generated by the pulsed arc plasma deposition (APD) technique as a catalyst for the formation of transmissible plasma-evolved graphene (TPEG). Physical vapour deposited catalysts favoured the formation of not only thin film coatings^{21,22} but also catalyst particles; therefore, they have been used for the preparation of catalyst particles for carbon nanotube (CNT) growth^{23,24}, including the synthesis of single-walled CNTs (SWCNTs)²⁵. Pulsed APD is a kind of physical vapour deposition in which a target element gets ionized with an applied pulsed bias voltage (**Supplementary Fig. 1**) and is then sputtered onto the substrate. For the formation of the TPEG herein, Co, Pt, Ir, W, and synchronous W and Co catalyst plasmas excited by pulsed APD with different bias voltages were irradiated onto suspended a-C for different sets of experiments (**Fig. 1a**,

Supplementary Table 1). Pt, Co, and Ir are widely employed catalysts for the synthesis of SWCNTs due to their high catalytic reactivity to C, where $\text{sp}^2\text{-C}$ is formed from carbon feedstock^{23,24}. Catalytically active W nanoparticles composited with C and Co (WC and Co_6W_7) have been utilized^{26,27} for the chiral-selective growth of SWCNTs. To probe the morphology of bimetallic CoW and its carbide catalysts employed for SWCNT growth, pulsed APD was used to deposit catalysts directly onto a TEM grid²⁸. When employing a catalyst plasma with bias voltages that are too intense or a grid pitch size that is too large (**Extended Data Fig. 10**), we found significant damage to the a-C mesh, which is the bottleneck for the TPEG technique, and a systematic investigation is needed. An a-C film held onto a PMMA support was further utilized to investigate that this process occurred at a significantly low temperature, and the effect of the soft support was investigated and compared to that for Cu or Mo (illustrated in **Fig. 1b**).

Raman spectroscopy is an important tool to identify graphene quality²⁹. The Raman spectrum of TPEG produced with **Protocol P1_Co** using a 50 mm pitch TEM grid showed that the Co plasma formed during pulsed APD with a bias voltage less than 100 V was not enough to form TPEG because the G band peak was not observed (**Fig. 2a**). The 2D peak induced by the second-order two-phonon process started to appear at 100 V in the Raman spectrum (**Protocol P2_Co**). These results indicate that nominal graphitization occurs under a bias voltage of 100 V or more. Upon increasing the bias voltage (140-250 V), a pronounced 2D peak appeared (**Protocol P3-P6_Co**), symbolizing the good quality of graphitic carbon²⁹ (**Fig. 2a, Extended Data Fig. 4a**). The smallest full width at half maximum (FWHM) of the Raman 2D and G peaks and the largest intensity ratio of the 2D band to the G band (I_{2D}/I_G) for 170 V (**Protocol P4_Co**) confirmed the good quality of the TPEG at this condition (**Fig. 2b**). There was significant damage in the central part of the mesh for a Co plasma with a voltage greater than 170 V (**Extended Data Fig. 10 (5,5), (5,6)**), and qualitative analysis of the Raman spectra taken at the remaining part showed a comparatively low-quality TPEG for high bias voltages (**Protocol P5-P6_Co**). In addition, when employing a TEM grid with a pitch larger than 75 μm , more than 90 percent of the a-C mesh was destroyed even with a Co plasma with a voltage of 170 V (**Extended Data Fig. 2b (Protocol P4_Co)**). TEM analysis performed for the Co deposited at 170 V onto a 50 μm a-C mesh on a Mo grid showed a high-quality graphitic carbon with almost no dark contrast areas that correspond to Co particles (**Fig. 2c**). Selected area electron diffraction (SAED) for this region showed the formation of polycrystalline graphite with favourable {110} and {112} orientations³⁰ (**Fig. 2d**). Bright-field scanning TEM (STEM) observations confirmed that they were composed of 3 to 12 layers of graphene (**Fig. 2e**). In very few places, nanoparticles with sizes larger than 10 nm were observed (**Fig. 2f, Extended Data Fig. 1a**) for the employed condition. Energy-dispersive X-ray spectroscopy (EDS) spectra and EDS mapping obtained for such an area (**Extended Data Fig. 1b-f**) showed that those particles were composed of Co covered with Mo particles. The reason for the formation of such particles is not clear, but the sputtered Co might have recombined with residual Mo on the a-C membrane because Mo comprised the a-C membrane support in the TEM grid. High-resolution TEM (HRTEM) analysis showed that the interlayer distance in the folded region of the 3.6 nm thick graphitic carbon was 0.34 nm (**Fig. 2f, g**), which confirmed the formation of

good quality graphene. The fast Fourier transformation (FFT) image (inset to **Fig. 2f**) taken within the blue rectangle in **Fig. 2f** shows that the stacking orientation was 101^{30} .

To probe the effect of the plasma exposure time, **Protocol P2'_Co** was employed, where the bias voltage was the same as that in **Protocol P2_Co**, but with 10 pulses. Optical microscopy (OM) is the easiest tool to identify graphene on SiO_2/Si^1 , so OM observation was performed for the TPEG produced with **Protocol P2'_Co** by transferring it onto SiO_2/Si after etching the Cu grid. Intensive care needed to be exercised while transferring the a-C membrane (thinner than 30 nm) onto the SiO_2/Si . The dark bluish circular area in the OM image (**Fig. 2h**) represents the mesh part of the grid, and the distinct colour variation indicates the formation of TPEG in the mesh part. During the transfer onto SiO_2/Si , crumpling of the TPEG was avoided for Raman mapping and atomic force microscopy (AFM) analysis. Raman mapping was performed within the red dotted rectangular area in **Extended Data Fig. 3a**. In the mesh part of the grid, the peak intensities for the G, 2D and D bands and their ratios ($I_{2D/G}$ and $I_{D/G}$) were uniform (**Extended Data Fig. 3b-e**). The uniform colour corresponding to the mesh part of the grid in the Raman G peak mapping (**Fig. 2i**) indicates the homogeneous graphitic nature of the TPEG, and the 2D peak intensity was pronounced in the central part (**Extended Data Fig. 3b**). This indicates that with increasing Co plasma exposure time, TPEG was formed, even at 100 V. Similarly, Raman mapping was performed on TPEG produced with **Protocol P3_Co**, where the bias voltage was 140 V (3 pulses of Co onto 75 mm pitch Cu grid). After transferring the TPEG onto SiO_2/Si , Raman mapping was performed and covered more than 80 percent of the mesh (red dotted rectangular area of **Extended Data Fig. 4b**). For the mesh part of the grid, the G, 2D and D band peak intensities and their ratios ($I_{2D/G}$ and $I_{D/G}$) were uniform (**Extended Data Fig. 4c-g**), similar to that for the TPEG produced by **Protocol P2'_Co** (**Extended Data Fig. 3b-e**). A pronounced 2D peak was seen in the combined spectrum obtained from the red rectangular part of the mapped image (**Extended Data Fig. 4h**). These Raman mapping results indicate the formation of homogeneous graphene layers. In addition, X-ray photoelectron spectroscopy (XPS) of TPEG produced with **Protocol P2'_Co** showed a narrowed FWHM for the C1s peak in the mesh-dominant area (~70 percent of the suspended part), further confirming the transformation of a-C into $\text{sp}^2\text{-C}$ (**Extended Data Fig. 2c, d**). It should be noted here that the intensity of the Co $2p_{3/2}$ peak was significantly reduced in the mesh-dominant part (details are discussed later). AFM analysis shows that an almost 3-fold reduction in thickness occurred after the transformation of a-C into TPEG around the mesh part of the grid (**Fig. 2j and Extended Data Fig. 2e-g**), although a nominal change in the thickness of the a-C membrane was also observed for the part supported onto the grid (**Extended Data Fig. 2e**). These results indicate that the a-C membrane in the mesh part of the grid was efficiently transformed into graphene by catalytically active Co plasma.

In addition, Co, Pt, Ir and W were used as plasma catalysts to form TPEG; Co has a high C solubility, while elements, such as Pt, Ir, and W, have a lower solubility than Co^{31,32}. In general, the desorption energy from the target material by plasma excitation depends on the element, which varies the intensity of plasmas generated even at an identical bias voltage. Therefore, the thickness of each element during the

deposition was monitored by a quartz crystal oscillator. The obtained results showed that the deposition rate decreased with the melting point; the deposition rate was the lowest for W and highest for Co (**Extended Data Fig. 5a**). To compare the catalytic activity, identical sets of experiments were run with these elements to form TPEG. The Raman spectra (**Extended Data Fig. 5b, d**) show a comparable quality for the TPEG with Ir and Pt. Qualitative analysis of the Raman spectra showed that the quality of the TPEG produced with Pt and Ir plasmas with a voltage of 170 V was the best herein (**Extended Data Fig. 5c, e**), which is consistent with the result for TPEG produced with Co. In contrast, the W plasma did not produce TPEG even with a bias voltage of 180 V, although the W deposition rate was almost equal to that of Ir at 170 V (**Extended Data Fig. 5a, 5f**). Upon increasing the bias voltage to 210 V and above, both the G band and D band appeared in the Raman spectrum, indicating the low catalytic activity of W. Upon increasing the plasma exposure time, both Pt and Ir produced good-quality TPEG even at 100 V, and the crystallinity was comparable to that for TPEG produced with Co at the optimal bias voltage (**Extended Data Fig. 6a, b**). OM images (**Extended Data Fig. 10**) show a significant difference in the morphology (wrinkles and waviness) of the a-C mesh in the central part and towards the edges of pitch with an increase in the bias voltage (70 to 170 V for Co, Ir, and Pt; and 100 to 250 V for W), providing an overview of TPEG formation. The a-C mesh starts to be destroyed from the central part due to an extreme increase in the stress with a bias voltage that is too high for Ir, Pt and W, as seen for the TPEG produced from Co (**Extended Data Fig. 10 (5,5), (5,6)**), and an identical trend can be seen for larger pitch grids.

It was very interesting to investigate TPEG formation using two elements with drastic differences in their catalytic activity, and the use of a synchronous Co and W plasma was the best choice because they show remarkable differences in catalytic activity for graphitization and C solubility^{31,32}. The bias voltage for Co was set to 70 V (instrumental lower limitation) and that for W was adjusted to make it equivalent to the voltage for other tested protocols (**Supplementary Table 1**). It is worth noting here that TPEG produced with **Protocol P2_Co+W** (140 V W and 70 V Co, each for 3 pulses) (**Fig. 3a**) was almost identical to that produced by a 140 V Co plasma only. This clearly indicates that the W plasma improved the catalytic activity of Co and vice versa. OM analysis further showed that after exposure to a 100 V W and 70 V Co plasma, the a-C mesh on a 100 μ m pitched grid was not destroyed, unlike for TPEG produced with **Protocol P4_Co** on a 100 μ m pitch grid (**Extended Data Fig. 2b, 10**) with a bias voltage of 170 V for Co. Upon increasing the bias voltage for W, a slight improvement in the TPEG occurred, and the W plasma at 180 V and Co plasma at 70 V were found to be best herein (**Fig. 3a, b**). Similarly, by increasing the plasma exposure time to 10 pulses for synchronous Co and W (**Protocol P1'_Co+W**), TPEG formation occurred even at low bias voltages (**Extended Data Fig. 6c**). TEM analysis of TPEG produced with **Protocol P1'_Co+W** showed graphitic features similar to those for TPEG produced with a 170 V Co plasma (**Protocol P4_Co**), but they were decorated with very dense nanoparticles (**Fig. 3c**). This observation was also consistent with TPEG produced with **Protocol P4_Co+W** that used a high bias voltage (240 V W and 70 V Co) (**Extended Data Fig. 7a, b**). HRTEM images taken within the blue and red rectangles in **Fig. 3c** show the formation of 3- to 12-layered graphene with an interlayer distance of 0.34 nm (**Fig. 3c-f**). Even after the transfer onto SiO₂/Si, both the OM image and Raman mapping performed on the mesh part of the grid show TPEG with a uniform quality (**Fig. 3h, i, Extended Data Fig. 8a-d**). The average Raman

spectra for TPEG obtained from the three different mapping regions show a pronounced 2D peak at the central part of the mesh and no 2D peak on the edge and outside part of the mesh (**Fig. 3j**). This clearly confirms that only the mesh part of the grid was transformed onto TPEG, and a-C supported onto the grid remained unchanged.

Furthermore, SWCNT nuclei that grew from different nanoparticles were observed in the TEM image (**Fig. 3c**) and are indicated by white arrows. Green and violet arrows point to areas containing other carbon structures that decorated the TPEG. This observation suggests that TPEG is not only appropriate for suspended graphene production but is also appropriate for the formation of three-dimensional (3D) hybrid structures composed of 0D, 1D and two-dimensional nanomaterials, which has potential applications ranging from energy storage to green energy production. SAED analysis showed the formation of polycrystalline graphite with preferred {110} and {112} orientations and WC with preferred 110 and 211 orientations^{30,33} (**Fig. 3g**). The interlayer distance of the lattice pattern (0.189 nm) measured for most of the particles revealed that those particles were WC with a 110 orientation³³. There is a possibility that Co- and W-based particles could have formed Co₆W₇, Co₆W₇C and WC particles, which would have acted as catalysts for the growth of SWCNTs²⁶⁻²⁸, but EDS and electron energy loss spectroscopy (EELS) characterization of the nanoparticles showed no presence of Co with a significant amount of W (**Extended Data Fig. 7d, e**), confirming the formation of WC. The absence of Co in the mesh part of the grid after an exposure to a W plasma with 70 V Co is analogous to the absence of Co for TPEG produced with Co only (TEM and XPS observation of **Protocol P2'_Co**), and we suspected that a significant amount of Co was transmitted through the mesh in both cases.

To investigate the possible transmission of Co and TPEG formation for TPEG produced with **Protocol P1'_Co+W**, XPS analysis was performed on the transferred sample with a focus on the detection area (diameter~0.2 mm), similar to TPEG produced with **Protocol P2'_Co**. The XPS spectra obtained for the mesh-dominant area and grid peripheral area showed an almost identically intense peak of W 4f_{7/2} (**Extended Data Fig. 8e, f**). However, compared with that for the peripheral part, the mesh-dominant part showed a significantly less intense Co 2p_{3/2} peak and more intense C 1s peak, which indicated that a significant amount of Co was transmitted through the mesh part of the grid, thereby transforming a-C into TPEG. This observation is identical to the XPS observation for TPEG produced with **Protocol P2'_Co** (**Extended Data Fig. 9b, c**).

To explore the plasma transmissibility in the TPEG, XPS analysis was performed by two separate sets of experiments. The TEM grids were held onto SiO₂/Si by maintaining a 0.5 mm gap during pulsed APD of Co, and they were exposed to a synchronous Co and W plasma with **Protocol P2'_Co** (100 V Co) and **Protocol P1'_Co+W** (100 V W and 70 V Co). OM analysis of the SiO₂/Si surface just below the TEM grid kept area showed traces of circular spots with an optical contrast identical to that outside the edge of the grid (**Fig. 4a, Extended Data Fig. 9a**). XPS analysis with a focused detection area (diameter~0.2 mm) was performed for the edge and the mesh parts of the Cu grid and the mesh-traced parts on SiO₂/Si of both samples. Relatively low intensity peaks in the Co 2p_{3/2} spectra from the mesh-traced part on SiO₂/Si were

observed for both experiment sets compared to those from other regions (**Fig. 4b, Extended Data Fig. 9c**). This indicates that relatively less Co plasma was recombined onto the SiO₂/Si after being transmitted through the mesh. However, the almost flat peaks of W 4f_{7/2} and 4f_{5/2} for the spectra obtained from the mesh-traced part on SiO₂/Si (**Fig. 4b**) indicate no transmission of W, which supports that WC nanoparticles were decorated on the TPEG obtained by identical sets of experiments. The C 1s peak in the spectra obtained from the mesh part of the grid decreased in width, supporting the successful transformation of a-C into TPEG in comparison to that for the other part.

The formation of only TPEG at the mesh part suggests that if a-C was supported on the materials softer than Cu or Mo, TPEG could be formed on them alike mesh on the TEM grid. To confirm this, 2-5 nm a-C deposited onto Cu by e-beam evaporation was transferred onto ~100 nm PMMA supported on SiO₂/Si, where PMMA was regarded as a soft support (**Fig. 4c**). Then, TPEG was formed by **Protocol P4'_Ir** (170 V Ir for 10 pulses) and **Protocol P4''_Ir** (170 V Ir for 5 pulses). OM and Raman analysis of TPEG produced with **Protocol P4'_Ir** and **Protocol P4''_Ir** showed that the a-C film on PMMA was transformed into TPEG with a maximum domain size of ~20 μm (**Fig. 4d-f, Supplementary Fig. 2**). In the case of TPEG produced on PMMA, the intensity ratio of the D band to the G band was higher than that of most of the TPEG produced from suspended a-C. To investigate the origin of the large D peak in the Raman spectra, monolayer graphene was synthesized by CVD and then transferred onto SiO₂/Si by a technique reported elsewhere³⁴. After CVD graphene on SiO₂/Si was annealed at 800°C under ultrahigh vacuum, it was exposed to an Ir plasma produced during pulsed APD. Raman analysis showed that the FWHM of the G band as well as the D peak intensity of the monolayered graphene significantly increased (**Supplementary Fig. 3**) after these treatments. This suggests that either lattice vacancies or non-crystalline regions formed on the graphene by plasma sputtering^{35,36}. We would like to note here that the TPEG formation process was not due to either Joule heating³⁷ or electromigration³⁸, but it was realized during the transformation of a-C into graphene by plasma-excited elements using pulsed APD.

In summary, by tuning the catalytic activity of a pulsed APD plasma, plasma-activated Co, Pt and Ir can transmit through a suspended a-C membrane or that on a soft support. During transmission through the membrane, not only did sp²-C bonding form but also its crystallinity drastically improved, and graphitization occurred. On choosing a plasma combination that pairs a catalytically active and less active plasma, a new 3D hybrid structure composed of fullerene (0D), CNTs (1D) and graphene (two-dimensional) materials was also realized, which could be applicable for energy generation purposes. This TPEG formation process is both time- and energy-efficient because less than 10 sec of exposure to a pulsed APD plasma produced TPEG, and each experiment lasted no longer than 30 min. The sustainability of PMMA as a supporting layer during the TPEG formation process further confirmed that the processing temperature was far below the melting point of PMMA (160°C), which is close to room temperature. This process is an avenue for the transformation of various amorphous materials into their crystalline structure, similar to the transformation of a-C into sp²-C.

Declarations

Acknowledgements We acknowledge the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan for support in the Private University Research Branding Project. A part of this work was conducted at the Nagoya Institute of Technology, supported by the Nanotechnology Platform “Molecule and Material Synthesis” of the MEXT.

Author contributions K.P.S. and T. M conceived the project. K.P.S. performed the TPEG experiments; characterized the materials by Raman spectroscopy, AFM, and XPS; and analysed most of the data. A.K.S. conducted the CVD graphene synthesis, OM observations and transfer of the graphene onto the SiO₂/Si. T.A. conducted the TEM observations. T.M. supervised the project. K.P.S. wrote the manuscript, T.M. revised it, and all authors commented on it.

Competing interests The authors declare no competing interests.

Additional information

Supplementary Information is available for this paper at....

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Methods

TEM grids

Commercially available TEM microgrids (Okensoji Co., Ltd., Japan) with amorphous carbon (a-C) membranes (~20-25 nm thickness) were utilized to form TPEG. For the TEM characterization of nanoparticles sputtered by physical vapour deposition, TEM grids with a-C membranes are widely used. The destruction of the suspended part of such a membrane during sputtering must be avoided. Our aim was to investigate the impact of sputtered plasma on the suspended a-C membrane window and the conditions to obtain TPEG. Cu grids (ELS-C10 with 100 μm pitch, and ELS-C075 with 75 μm pitch), Mo grids (ELS-M05 with 50 μm pitch) and quantifoil R0.6/1 Cu grids (M2947C) were employed. During the pulsed APD process, the TEM grids were directly held onto the stages of the pulsed APD system with the a-C membrane-coated side facing up.

Amorphous carbon membrane preparation

Carbon was deposited (~2-5 nm) onto the Cu foils by electron beam deposition in an ultra-high vacuum chamber. Carbon tablets (F10Xt5, 3623703) purchased from Kojundo Chemical Laboratory were used as the target. The rate of deposition was investigated by using a quartz crystal thickness monitor. Thin a-C films deposited onto the Cu foils were further transferred and processed with the PMMA support.

Pulsed arc plasma deposition

A pulsed APD system (APD-2S, Advance Riko, Inc. Japan) was used to produce the catalytic plasma that was exposed to the a-C membrane. Co, W, Ir, and Pt were used separately as targets during the pulsed APD processes. Synchronous sputtering of a Co and W plasma was also performed to investigate the combined effect of this plasma. The substrate was kept 8 cm away from the target on the stage. Pulsed APD was performed under a vacuum of 5×10^{-4} Pa in the chamber, which was evacuated using a turbo molecular pump. The frequency of the pulsed APD process was set at 3.0 Hz for all 29 protocols used in this research (**Supplementary Table 1**). The thickness of each element was investigated using a quartz thickness crystal monitor (**Extended data Fig. 5a**).

Transfer of a-C membrane and TPEG onto arbitrary substrates

A thin PMMA layer was spin coated onto a-C/Cu, and PMMA/a-C was detached from Cu by an electrochemical delamination process. A solution of 0.1 N NaOH was used as the electrolyte, Pt was used as the anode and hydrogen bubbles were produced at the a-C and Cu interface in the counter electrode, which was used as the cathode. The PMMA/a-C was flipped and transferred onto SiO₂/Si, which was used as a substrate for pulsed APD. After pulsed APD, a thin a-C film was transformed into TPEG, and there was a noticeable difference in the attachment between the TPEG/PMMA membrane on SiO₂/Si and that of a-C/PMMA, although flipping the membrane was straightforward. TPEG/PMMA was further flipped and transferred onto SiO₂/Si, and then PMMA was removed by dipping into hot acetone.

Typical samples of a-C on Cu TEM grids (after pulsed APD) were held onto FeCl₃ solution to etch the Cu grid. The suspended membrane was cleaned in deionized water and transferred onto SiO₂/Si. Special care was taken for the transfer of a very thin (<30 nm) membrane, which was done as soon as Cu was etched.

Optical microscopy characterization

An optical microscope was present in the Raman system (RAMANForce, Nanophoton), and 3D laser scanning confocal microscopy (Keyence, VK-X series) was also employed to acquire OM images in this research. The former OM images were black and white (B/W), while the latter were coloured. For the identification of physical damage to the suspended membrane, the B/W images were used. The impact of various plasmas (protocols with S. N. 1-27) on the 50, 75 and 100 μ m pitch TEM grids are summarized in **Extended Data Fig. 10**. OM has been utilized as the best tool for the identification of graphene. The optical contrast of graphene is distinct on SiO₂/Si based on the number of layers. The TPEG obtained in this research was dark blueish in colour compared to the colour of the a-C when it was kept on SiO₂/Si.

Raman measurement

A Raman system (RAMANForce, Nanophoton) was employed in which a 532 nm excitation laser and x100 objective lens were used. An excitation light with a laser power of less than 0.2 mW was used to

illuminate the observation point to avoid excess heating. The exposure time was 30 sec with averaging every 10 sec for a total of 3 times, and the slit width was $\sim 50\text{ }\mu\text{m}$. For Raman mapping, we used $0.5\text{ }\mu\text{m}$ steps for 4 sec exposures with averaging every 2 sec for a total of 2 times. Prior to the measurement, a charged coupled-device (CCD) camera was cooled to -70°C , and the Raman shift was calibrated using the Si phonon peak at 520 cm^{-1} of the Si wafer. For quantitative Raman analysis, Raman spectra of the TPEG produced onto a $50\text{ }\mu\text{m}$ pitched Mo grid were utilized.

XPS measurement

The chemical composition of the a-C membrane and TPEG was characterized using XPS (JPS-9200, JEOL, Japan). We used a Mg K_{α} excitation source (1253.6 eV) with a spot size of $200\text{ }\mu\text{m}$. The XPS analysis was performed in an ultrahigh vacuum (UHV) chamber that was kept under $6\times 10^{-7}\text{ Pa}$ during the XPS measurement. Survey spectra were taken with a pass energy of 100 eV with a step energy of 1.0 eV. C 1s, Co 2p and W 4f spectra were measured with a pass energy of 20 eV with a step energy of 0.1 eV. The binding energy of each peak was calibrated by using the Si 2p peak of SiO_2 (Si^{4+} : 104.5 eV) and confirmed by the C 1s peak (384.5 eV).

AFM characterization

AFM was performed for TPEG/ SiO_2 /Si using an atomic force microscope (Smart SPM-1000, Horiba, Japan) equipped with an AFM-Raman System (Horiba Scientific). A carbon nanofibre tip cantilever (Olympus, OMCL-AC160TS) with a force constant of 26 N/m and resonating frequency of 300 kHz was used to scan the surface in alternating current (AC) mode. **Fig. 2j** and **Extended Data Fig. 2e-g** show that the TPEG was significantly thinner ($\sim 9\text{-}11\text{ nm}$, corresponding to suspended a-C regions) than the a-C part ($\sim 20\text{-}25\text{ nm}$, corresponding to Cu grid regions), which indicates that transmission of the catalytic plasma through a-C changed it into crystalline carbon, resulting in a significant reduction in its thickness. It is quite not clear whether a significant amount of carbon was transmitted with the catalyst itself.

TEM characterization

TEM was performed (JEM ARM 200F, JEOL, Japan) on an instrument operated at 200 keV. Annular dark field (ADF) images were obtained using STEM, and atomic-resolution EDS analysis was also performed to identify the atomic compositions. EELS was also performed for a precise identification of the atomic compositions.

Data availability

The datasets generated and/or analysed that support the findings in this study are available from the corresponding authors on reasonable request.

Figures

Figure 1

Schematic diagram of formation of TPEG. a) Schematic illustration of TPEG formation by utilizing an a-C membrane on a commercial TEM grid. Upon transmission through the suspended a-C, a catalytic plasma can transform the a-C into graphene. Dual catalytic metal plasmas (one with high transmission ability and the other with low transmission ability) and simultaneous irradiation can leave nanoparticles on the graphene. b) Schematic illustration of TPEG formation by utilizing a-C/poly (methyl methacrylate) (PMMA). PMMA can act as a soft support for a-C so that catalytic plasma can be transmitted through the a-C and become condensed away from a-C layer.

Figure 2

Catalytic properties of Co plasma as a function of the applied bias voltage. a) Typical Raman spectra taken from an as-produced TPEG produced with a 3.0 Hz Co plasma for 3 pulses at different bias voltages. b) Summary of the intensity ratio of the D band to G band (I_D/I_G), that of 2D band to G band (I_{2D}/I_G), 2D FWHM and G FWHM of TPEG produced with a 3.0 Hz Co plasma for 3 pulses at different bias voltages. HRTEM analysis of TPEG produced with Protocol P4_Co. c) HRTEM micrograph. d) SAED taken around Fig. 2(c), where the inset is the spectrum across the dotted green line obtained using Gatan software. The hkl indices in parentheses indicate the orientation of the graphite. e) Bright-field STEM image across the folded area. f) HRTEM micrograph. The black region is a nanoparticle in a folded region of the TPEG. The inset is the FFT image that was taken for the area within blue rectangle. g) Interlayer distance measured within the blue dotted rectangle in Fig. 2 (f). h) OM images of TPEG produced with Protocol P2'_Co transferred onto SiO_2/Si , where the dark blue circular parts represent the mesh parts in the TEM grid. i) Raman mapping of G band peak intensity within the dotted rectangular area in Extended

Data Fig. 3(a). j) 3D atomic force microscopy image (two-dimensional image is Extended Data Fig 2e) of region within red square in Fig. 2h.

Figure 3

Catalytic properties of Co and W plasma as a function of applied bias voltage. a) Typical Raman spectra taken from as-produced TPEG with synchronous 3.0 Hz Co and W plasma for 3 pulses at different W bias voltages with 70 V Co. b) Summary of the intensity ratio of the D band to G band (I_D/I_G), that of the 2D band to G band (I_{2D}/I_G), 2D FWHM and G FWHM of TPEG produced with synchronous 3.0 Hz Co and W plasma for 3 pulses, where each had a different W bias voltage. HRTEM analysis of TPEG produced with Protocol P1'_Co+W. c) HRTEM micrograph. d) and e) High-resolution images of the areas within the blue and orange rectangles. White (SWCNT nuclei), green (carbide/graphene), and violet (fullerene) arrows indicate the various nanostructures that were observed. f) Interlayer distance measured within the blue dotted rectangle in Fig. 3 (e). g) SAED taken in the area in Fig. 3(c). The hkl indices indicated in white and black parentheses show the orientations of the graphite and WC, respectively. h) OM images of another TPEG produced with Protocol P1'_Co+W that was transferred onto SiO_2/Si ; the dark blue circular areas

represent the mesh part of the TEM grid. The inset is the OM image from a typical area in Fig. 3 (h) where the Raman mapping was performed (within the dotted rectangular area). i) Raman mapping from within the dotted rectangular area in the inset of Fig. 3 (h). j) Combined Raman spectra highlighted in different colours that are identical to the rectangular regions indicated in maps in Fig. 3 (i).

Figure 4

TPEG with a soft support. a) OM images of the TPEG produced with Protocol P1'_Co+W on the 75 μm carbon mesh on a Cu grid (Right) and pulsed APD Co on SiO₂/Si through the mesh part of the grid (left). An approximately 0.5 mm gap was maintained between the Cu grid and SiO₂/Si by using Kapton (polyimide) tape. b) C1s, Co2p_{3/2}, and W4f XPS spectra obtained for the edge part, the mesh part and the mesh-traced part onto SiO₂/Si, which are highlighted with their respective colours (Extended Data Fig. 9d shows the survey spectra). TPEG with PMMA support. c) Photograph of a-C on PMMA/Cu and graphene produced with Protocol P4''_Ir that was transferred onto SiO₂/Si after etching Cu. PMMA was utilized as a soft support. d) Raman spectra measured at various points on the TPEG before removing the PMMA (6 different spectra were randomly taken). e) OM image of graphene after transferring it onto SiO₂/Si. f) Raman spectra observed at different points in Fig. 4 (e) that are labelled with their respective colours.

Supplementary Files

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- [Sharmaetal.2020roomtemperatureAPDgrapheneNature20201007supplementary.docx](#)