Chemical vapour deposition of freestanding sub-60 nm graphene gyroids
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The recent literature highlights the promise of such porous, 2D materials not only offer unique functionality as planar atomically thin layers but can also be engineered into complex 3D structures, allowing the design of a new class of materials with tailored mechanical, thermal, electrical, and optical properties, ultra-low densities, and high surface areas. The direct chemical vapour deposition of freestanding graphene gyroids with controlled sub-60 nm unit cell sizes is demonstrated. Three-dimensional (3D) nickel templates were fabricated through electrodeposition into a selectively voided triblock terpolymer. The high temperature instability of sub-micron unit cell structures was effectively addressed through the early introduction of the carbon precursor, which stabilizes the metallized gyroidal templates. The as-grown graphene gyroids are self-supporting and can be transferred onto a variety of substrates. Furthermore, they represent the smallest free standing periodic graphene 3D structures yet produced with a pore size of tens of nm, as analysed by electron microscopy and optical spectroscopy. We discuss generality of our methodology for the synthesis of other types of nanoscale, 3D graphene assemblies, and the transferability of this approach to other 2D materials. Published by AIP Publishing.
connected polystyrene (PI), poly(ethylene oxide) (PEO), and polystyrene (PS) blocks. \(^2^2\) ISO of different molecular weights was used to obtain polymer templates with different unit cell sizes. Polymer gyroids with unit cell sizes of \(\sim 35\)\,nm and \(\sim 60\)\,nm were fabricated using ISO of \(\sim 33\)\,kg/mol and \(\sim 80\)\,kg/mol, respectively. \(^2^4\) They were deposited on conductive fluorine-doped tin oxide (FTO)-coated glass and thermally annealed in a vacuum oven to form the desired microphase-separated morphology. PI was subsequently removed from the ISO polymer templates by UV exposure and an ethanol rinse. These polymer templates were then metallized by electroplating Ni into the voids left after PI removal, using the FTO-coated glass as a working electrode. The remaining polymers were subsequently removed by oxygen plasma etching. Polymer removal resulted in gyroidal Ni network. (b) Nickel gyroid prepared by electroplating into the empty space left after polystyrene removal. (c) Nickel gyroid covered in graphene after CVD with the acetylene precursor. (d) Self-standing graphene gyroid after nickel removal with ferric chloride solution. The insets show cross-sections of the respective gyroid along the indicated white lines.

Figure 2 shows SEM analysis of the gyroid structure at the various process stages. CVD allows the fabrication of freestanding graphene gyroids across large areas. As shown in Fig. S.I(b) (supplementary material), graphene gyroids can already be fabricated over cm\(^2\) areas. Optically, freestanding graphene gyroids are similar in appearance to the nickel templates although they appear more transparent [Figs. S.I(a)–S.II(d), supplementary material]. SEM images show that both G60\(_G\) and G35\(_G\) have inherited the shape and scale of their respective nickel templates—G60\(_N\) and G35\(_N\), with unit cells of \(\sim 60\)\,nm and \(\sim 35\)\,nm (Figs. 2(a)–2(f), respectively). Energy dispersive X-ray spectroscopy (EDX) [Fig. S.II(e), supplementary material] show no Ni peak, consistent with the removal of Ni. The O, Si, and Sn peaks in the graphene gyroid EDX spectrum originate from the underlying FTO glass and are more prominent than for the nickel gyroids due to the higher electron and x-ray transparency of the graphene gyroids. \(^2^8\)\(^,^2^9\) Nickel X-ray excitation energies are K\(_X\) = 7.480 keV and L\(_X\) = 0.849 keV. With 12\,kV acceleration energy, the L\(_z\) peak is prominent and the K\(_X\) peak is weak. These peaks are not observed at all in the EDX spectra of the graphene gyroids. The graphene gyroids display good electrical properties—\(\sim 500\)\,nm thick G60\(_G\) transferred on non-conductive glass exhibited a sheet resistance of 240\,\Omega/sq (see supplementary material for details).

The Raman spectra in Fig. 3(a) compare G60\(_G\) deposited with a maximum process temperature of 650\,°C, with graphene deposited under similar conditions on Ni foam (\(\sim 100\,\mu\text{m} \) pore size), \(^1\) Ni foil (25\,\mu m thick) and Ni film (500\,nm thick), with the major difference being the heat conductivities and thicknesses of the substrates. G60\(_G\) is also compared with G35\(_G\) deposited with a lower maximum process temperature (550°C). The Raman spectra of
graphene deposited on 3D gyroidal structures differ significantly from those of the graphene deposited on flat substrates despite very similar growth conditions. The Raman spectra of the foam, foil, and film are characteristic of flat, few-layer graphene.\(^{30}\) In contrast, the spectra of G60\(_G\) and G35\(_G\) display prominent and wide D and G peaks with an intensity ratio (I\(_D\)/I\(_G\)) of ~1. The prominence of the D peaks in both G60\(_G\) and G35\(_G\) is attributable to the presence of many small and disordered graphene domains.\(^{31,32}\) The G band for G60\(_G\) and G35\(_G\) is grown at lower temperatures, recrystallization, self-healing, and merging of domains could not happen to the same extent as in G60\(_G\) (discussed further below). Consistent with the Raman results discussed above, a higher nucleation density to minimise the surface area, enabled by the increase in Ni self-diffusion with temperature.\(^{37}\) Using a typical one-step CVD process,\(^{18}\) where the hydrocarbon precursor is introduced only once the growth temperature has reached, both G35\(_Ni\) and G60\(_Ni\) do not preserve their original morphologies and transform into large clusters already during the heating ramp [Fig. 4(a)]. To overcome this limitation, we introduce the carbon precursor right from the beginning of the heating ramp (predosing), which helps to stabilize the nickel templates and prevents the formation of Ni clusters at the growth temperature [Fig. 4(b)]. The formation of clusters is driven by the thermodynamic tendency to minimise the surface area, enabled by the increase in Ni self-diffusion with temperature.\(^{37}\) Using a typical one-step CVD process,\(^{18}\) where the hydrocarbon precursor is introduced only once the growth temperature has reached, both G35\(_Ni\) and G60\(_Ni\) do not preserve their original morphologies and transform into large clusters already during the heating ramp [Fig. 4(a)]. To overcome this limitation, we introduce the carbon precursor right from the beginning of the heating ramp (predosing), which helps to stabilize the nickel templates and prevents the formation of Ni clusters at the growth temperature [Fig. 4(b)]. The following mechanisms may play a role in stabilising the template: During the initial heating of the template, precursor dissociation begins well below the maximum process temperature, with the supplied C being readily absorbed by the Ni template, given the reasonably large solubility of C in Ni.\(^{38}\) When the Ni surface becomes saturated, the additional hydrocarbon dissociation feeds graphene nucleation at the Ni surface.\(^{39}\) The relatively small bulk of the gyroids compared to thicker catalyst foams, foils, and films means that this point is reached at a lower temperature. Consistent with the Raman results discussed above, a higher nucleation density is thus expected as a result of the lower C diffusivity at this low nucleation temperature.\(^{18}\) as well as the higher template curvature and thus an abundance of low-coordination sites which serve as preferential graphene nucleation sites. This
promotes the formation of small graphene islands of low graphitic quality which continue to grow isothermally as the precursor exposure continues to form a continuous graphitic network over the template. These graphitic deposits are expected to exhibit a strong interaction with Ni, as a result of hybridisation between the graphene π and Ni 3d orbitals, thus helping to stabilise the template. Additionally, nickel surface carbides are known to readily form at temperatures below 500°C, which may also assist in stabilising the template. As the process temperature continues to increase, amorphous and highly defective regions of the C coating are graphitised, which may involve defect healing and a redissolution process, as the C solubility in Ni increases with temperature. This ultimately yields the crystalline graphitic layers shown in the TEM images of Fig. 3.

Our approach can be extended both to other metal templates and to materials beyond graphene. The suitability of a given metal template will depend on its catalytic efficiency to induce graphitisation compared to its self-diffusivity at the given CVD temperature. Hence, the temperature instabilities of sub-micron unit cell structures can be similarly addressed for metals that in those respects show a similar behaviour to Ni, such as Co, or for metals, which require higher growth temperatures but have lower self-diffusivities, such as Pt. For metals, such as Cu, which require higher temperatures for graphene growth and have high self-diffusivities (3 orders of magnitude higher for Cu than Ni at 900°C), successfully applying our approach may be more challenging. Nonetheless, there are further avenues to increase template stability, for instance, by plasma pre-coating. The challenge for 3D structural control is common to many different materials beyond graphene, including for instance ceramic foams. Ceramic foam structures, particularly those based on thermally and chemically stable boron nitride, have a wide application potential, ranging from mechanical metamaterials to filtration and catalysis. The templated CVD approach can be extended to fabricate freestanding hexagonal boron nitride (h-BN) gyro structures. The template stabilisation for h-BN CVD is more complex to rationalise as the supply, solubility, and chemical behaviour of both B and N with respect to the catalyst template have to be considered. This connects to our previous detailed h-BN growth studies, but an in-depth discussion of this goes beyond the scope of this paper. Similarly, without discussing the specific growth mechanisms involved, our approach can be extended to transition metal dichalcogenides, for instance, by using Au gyroids for WS2 CVD.

In summary, we demonstrate the controlled fabrication of graphene gyroids with sub-60 nm pore-sizes, produced by an optimised CVD process using Ni templates which were generated by electrodeposition into a selectively voided triblock terpolymer. The resulting freestanding graphene gyroids of two unit cell sizes, 35 nm and 60 nm, faithfully replicate the original polymer structure and show reasonable graphitic crystal quality with wall thicknesses below 15 layers. The early introduction of the carbon precursor suppressed the high temperature instability of sub-micron network morphologies. This approach can be extended to other metal templates and to materials beyond graphene. For a given template, this approach relies on its catalytic efficiency being sufficient to induce 2D material growth at temperatures where self-diffusivity is low enough that the structure remains stable. The demonstrated control of such foam-like materials on the sub-micron scale offers new or enhanced functionalities for a wide range of emerging applications where light-weight, high surface area, and mechanical stability are desirable.

See supplementary material for a detailed description of materials and methods, and additional data on graphene gyroids and pyrolytic conversion of the polymer template.

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FIG. 4. Process diagrams presenting unstable (a) and stable (b) procedures for graphene gyroid preparation. The structures in (b) were stabilised by acetylene (gas precursor) preloading at RT. SEM images in (a) show damage to G35 and G60 at as low as 500°C and 600°C, respectively. SEM images in (b) show preserved G35_G and G60_G after processing at 550°C and 650°C, respectively. The process diagram in (b) also shows the optimal conditions for graphene gyroid preparation by CVD.

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