# Chemical Tailoring of Functional Graphene-Based Nanocomposites by Simple Stacking, Cutting and Folding

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*T*hanks to their outstanding electrical, optical, chemical, mechanical and thermal properties, graphene and its 2D analogues hold a great potential for numerous technological applications in diverse fields including electronics, sensing, energy conversion and storage as well as in nanocomposites and desalination membranes.[1,2] When 2D materials are combined (as fillers) with polymers to form macroscopic composites, they enable to boost the chemical and physical properties of the latter. Such properties enhancement can be achieved and maximized only when the 2D materials are uniformly/homogeneously distributed in the polymer matrix at the very nanoscale.[3] The final performance of nanocomposites therefore does not only depend upon the inherent properties of the 2D materials, but it is also severely affected by how they are dispersed in the polymer matrix, their interface engineering, stress transfer and morphology control on the nanoscale.[4] In this regard, it is particularly important to take full advantage of the enormous aspect ratio and specific surface area possessed by 2D materials which are unique characteristics that greatly contribute to confer them exceptional functions. However, the optimization of the interface between 2D materials and polymers is a very challenging task. The main obstacle is the strong propensity of 2D materials to undergo aggregation during their processing,[5] hindering in this way the full exploitation of their superb properties which are best expressed when the flakes are isolated. When 2D materials are combined with a given polymer to form composites, such aggregation determines a poorly efficient stress transfer between polymer matrix and fillers, ultimately deteriorating the final performance of nanocomposites. Graphene, with a Young's modulus of 1 TPa and intrinsic tensile strength of 130 GPa,[6] is hundred times stronger than steel. On the same time, it is highly flexible and stretchable. As a result, graphene has already been widely combined with polymers by making use of covalent or non-covalent approaches to fabricate high performance nanocomposites, via solution mixing, melt blending, electrospinning, layer-by-layer or *in-situ* polymerization, *etc*.[7] Despite the intensive research progress in the field of graphene based nanocomposites, achieving a full control over the structures and tuning the properties of materials across multiple length scales to ultimately create mechanically robust nanocomposites remain major challenges. Writing in *Science*,[8]

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Strano and co-workers described an elegant modular approach which relies on controlled stacking, cutting and folding to generate aligned and robust graphene/polycarbonate (G/PC) composites. A large area graphene sample grown on copper by chemical vapour deposition (CVD),[9] is covered by a spin-coated PC film (having thicknesses ranging from several hundred nanometres to a few micrometres, depending on the concentration used). PC was chosen as polymer matrix in view of its transparency and mechanical strength. The chemical etching of the Cu support leads to a freestanding ultrathin film consisting of a large area single-layer graphene coated by a PC layer. Such bi-component films can be stacked, cut into four parts, then stacked again and finally hot-pressed to obtain planar G/PC nanocomposites (Figure 1a). Significantly, such nanocomposites can be made of as many as 320 parallel layers with thickness ranging from 0.032 to 0.11 millimetres. At an extremely low volume fraction of only 0.082%, the nanocomposites show significantly increases in the effective elastic modulus and strength, with an increased stiffness up to 30% compared with the PC control. The reinforcement in this case is attributed to the direct load transfer to the graphene fillers, which differs from the case when graphene oxide (GO)/functionalized graphene is employed to stiffen a polymer matrix by primarily tailoring strong interfacial interactions between the two components.[3] At a volume fraction of graphene at $V_G \approx 0.185\%$, the nanocomposite displays an anisotropic electrical conductivity as high as 417 S m$^{-1}$ (PC itself is insulating). Furthermore, the composites also show a high optical transmittance value of 98% per layer, with 90% at 9 layers and 58% at 36 layers, obeying the Lambert-Beer law.
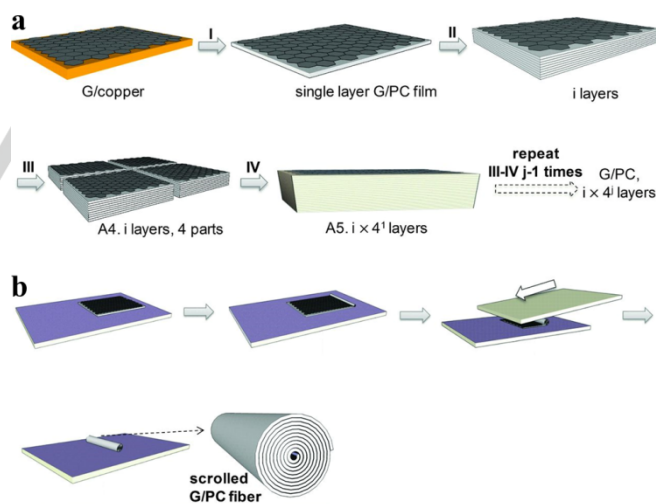


**Figure 1.** Fabrication of G/PC nanocomposites. a) The stacking and cutting method: I) spin-coating PC film onto graphene and etching away copper; II) stacking G/PC layers; III) cutting G/PC layers into four parts; IV) stacking and hot-pressing. III-IV steps can be repeated many times to obtain thicker films. b) The folding method: transverse shear method was used for the fabrication of scrolled nanocomposite fibre. Adapted from reference 8 (Copyright AAAS, 2016).

Furthermore, Archimedean spiral (scroll-shaped) fibres can be prepared by an analogous transverse shear scrolling method

involving internal axial rotation and interlayer translation (Figure 1b). The two scrolled fibres (fibre 1 and fibre 2, with a diameter of ≈ 105 and 160 µm, at $V_G$ ≈ 0.185% and 0.082%, respectively) show higher uniaxial tensile storage modulus (E', measuring the stored energy and representing the elastic portion) and loss modulus (E'', measuring the energy dissipated as heat and representing the viscous portion), and also ultimate tensile strengths (the capacity of a material/structure to withstand loads tending to elongate) than the PC control. For example, the ultimate tensile strength of fibre 1, fibre 2 and the PC control is 160, 135 and 120 MPa, respectively. The fibres show exotic, telescoping elongation at break as high as 110%, being 30 times greater than Kevlar. Interestingly, these artificial scrolled fibres can also retain anisotropic electrical conduction along the graphene planar axis and transparency. Therefore, these composites hold great potential for substantial mechanical reinforcement, electrical, and optical properties at very low volume fractions.

The approach and results reported by Strano and co-workers are very appealing. Yet, some unsolved challenges need to be addressed to exploit the full potential of 2D materials as key components in nanocomposites. For application on industrial scale, the production and processing of 2D materials with a reasonable cost, at sufficient quality and quantity still need to be proven. Growth of large area, high purity, uniform and defect-free graphene films using CVD approach is still far beyond satisfaction. For example, wrinkles, grain boundaries and other type of defects are normally present in the graphene films.[9] How these features affect the interaction with a polymer matrix and further the performance of nanocomposite, still need to be answered. Importantly, fundamental research in processing (interface engineering and morphology control), multiscale characterization, and analysis/modelling is required in order to optimize the structural and functional properties of graphene-based nanocomposites.

Despite the various obstacles to be overcome in the future, the work by Strano and colleagues has well demonstrated that nanoscale engineering is quite a promising strategy to produce composites with outstanding properties. The combination of graphene with polymer for composites applications allows to study fundamental chemical and physical properties of nanostructured materials by unravelling structure/property relationships, and holds also a clear technological relevance. The stacking, cutting and folding approach can be exploited in the field of graphene/other 2D materials as fillers and also different kinds of polymers for nanocomposites with *ad-hoc* functions. When one wants to create composites with unique mechanical properties, homogenous dispersion of fillers in polymer matrix and strong interfacial interaction between fillers and polymers are absolutely required for optimal reinforcement. A potential next step will be to introduce some functional groups on CVD graphene, which can enhance the interfacial interaction and lead to stronger adhesion between graphene and polymer matrix via non-covalent forces (e.g., hydrogen bonding or electrostatic interactions). The unique combination of high axial, tensile stiffness and strength coupled with a very high flexibility suggests that a layer-by-layer stacking of the 2D materials within the polymer to form the composite should greatly contribute to the improved properties of the latter and may offer maximal

exploitation of the unique anisotropic mechanical properties of the 2D materials. Nevertheless, this point should still be further demonstrated. The other viable approach to best process the nanocomposites is to covalently attach polymers on CVD graphene using *in-situ* polymerization, when a high electrical conductivity of the nanocomposites is not required. The method presented by Strano and co-workers cleverly avoids the aggregation of graphene, and it makes it possible to precisely control the interface between graphene and polymer. As a result, it holds potential as functional foam and coating for applications in aerospace, electronics, energy storage, optical devices, electromagnetic Interference (EMI) shielding, sport goods, defence layer, *etc*. In this sense, the contribution by Strano and co-workers will be of widespread interest in the chemistry community as it provides new insight which will likely have significant impact in future developments in a field at the cross-road between chemistry of complex matter and nanotechnology.

## Acknowledgements

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