Layered and scrolled nanocomposites with aligned semi-infinite graphene inclusions at the platelet limit

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Two-dimensional (2D) materials can uniquely span the physical dimensions of a surrounding composite matrix in the limit of maximum reinforcement. However, the alignment and assembly of continuous 2D components at high volume fraction remain challenging. We use a stacking and folding method to generate aligned graphene/polycarbonate composites with as many as 320 parallel layers spanning 0.032 to 0.11 millimeters in thickness that significantly increases the effective elastic modulus and strength at exceptionally low volume fractions of only 0.082%. An analogous transverse shear scrolling method generates Archimedean spiral fibers that demonstrate exotic, telescoping elongation at break of 110%, or 30 times greater than Kevlar. Both composites retain anisotropic electrical conduction along the graphene planar axis and transparency. These composites promise substantial mechanical reinforcement, electrical, and optical properties at highly reduced volume fraction.

The concept of nanocomposites is motivated by the observation that filler particles can stiffen and strengthen otherwise softer materials such as polymers to form lightweight, sturdy composites. Eschelby (1) first demonstrated this possibility mathematically for ellipsoidal “inclusions” in a solid. In practice, however, it has proven exceedingly difficult to insert closely spaced but distinctly separated nanoparticles within a material, a fundamental requirement for strengthening it. For anisotropic nanoparticles, such as platelets, nanofibers, or nanotubes (2, 3), mechanical reinforcement can occur at very low volume fractions of the added filler, because the particles can align along preferential axes of strain (4–6). For a platelet filler such as graphene or other two-dimensional (2D) materials, however, a unique limit can be realized as the aspect ratio, a, of the aligned plates approaches infinity. A closely spaced stack of aligned, semi-infinite plates of nanometer or atomic thickness approaches the limit of maximal mechanical reinforcement at minimal platelet addition per mass of material. It has only recently become possible to test this $a \to \infty$ limit with the development of chemical vapor deposition (CVD) methods of creating single-unit cell- or atom-thickness films, such as graphene (7, 8) and other 2D materials (9) that can span the physical dimensions of a composite large enough for testing. In this work, we introduce two fabrication methods that can take a thin layer of molecular thickness and construct large composite stacks that scale exponentially with the number of processing steps. An analogous shear scrolling method creates Archimedean scroll fibers from single layers with similar scaling. The methods produce materials that demonstrate the $a \to \infty$ limit while combining electrical and optical properties at minimal volume fraction of the filler.

The planar stacking method generates a thickness that exponentially scales with each successive quadrant fold or segmentation, $j$, as $4^j$. Further hot-pressing promotes the interlayer integration (Fig. 1A). Replicating the process $j$ times generates a nanocomposite of $i \times 4^j$ layers and a lateral dimension of $W/4^j$, where $i$ is the initial stacking or number of layers and $W$ is the initial width of the $i$-layer composite (Figs. 1, B to D). We use polycarbonate (PC) as the polymer matrix due to its transparency and mechanical strength, creating bulk composites from CVD monolayer, polycrystalline graphene (10) (Fig. 2A) with layer numbers of 8 to 320 and volume fractions ($V_{G}$) of 0.003 to 0.185% (figs. S1 and S2 and table S1). The graphene layers appear intact upon this processing because the size of the translucent area containing graphene exhibits little change after each pressing step. Raman spectroscopy (Fig. 2, B and C, and fig. S3) confirms that the absolute intensity of the graphene 2D peak ($I_{2D}$) decreases with increasing layer number, approximately following the Lambert-Beer law (fig. S3C and supplementary text 1).

$$-\log(I_{2D}/I_{0}) = kl + c$$

The equation is verified by well-fit least-squares regression of these data for graphene/polycarbonate (G/PC) composites of $V_{G} = 0.030\%$ and of $V_{G} \approx 0.009\%$, each ranging from 1 to 144 layers (Fig. 2C). The differences between the two fitted curves are very small due to the very low extinction coefficient ($< 0$) of the highly transparent PC layer. The composites have high optical transmittance of 90% at 9 layers and 58% at 36 layers, following the Lambert-Beer law (fig. S4), corresponding to a transmittance of 98% per layer, in agreement with the known visible light transmittance of monolayer graphene (11). We also found an alternate route to stacked, planar composites by monomer impregnation and in situ polymerization within expanded graphite derived from the thermal treatment of iodine chloride-intercalated highly ordered pyrolytic graphite (12), achieving up to $V_{G} = 0.60\%$ (fig. S5). However, the quality and control of layer spacing for the resulting composite was found to be lower than the $4^j$ method (fig. S5E).

We also use an analogous stacking procedure to create Archimedean spiral fibers (Fig. 1, E to I, and figs. S6 to S8). A transverse shear force scrolls a single G/PC film ($2.0 \times 2.2$ cm) into a fiber (Fig. 1E) of diameter $105 \pm 2$ μm (fiber 1) measured optically (figs. S6 and S7) and $160 \pm 4$ μm (fiber 2) (Fig. 1F and figs. S6 and S8). The layer spacing of $180$ and $410$ nm, respectively, induces an observable multilayer thin-film interference in Fig. 1F (and fig. S6, B and C, respectively). The fiber axial cross section has a deformed spiral structure (Fig. 1, G to I, and fig. S9). Both methods can control the resulting $V_{G}$ over three orders of magnitude from 0.003 to 2.55% (table S1).

Despite having vanishingly small $V_{G}$, such aligned composites demonstrate substantial increases in both the uniaxial tensile storage moduli ($E'$) and loss moduli ($E''$) from dynamic mechanical analysis (DMA) (Fig. 3, A and B). Two $4^j$ planar samples with $V_{G} = 0.082$ and 0.185%, respectively, both at 40 layers, have significantly higher $E'$ than pure PC controls (Fig. 3A), with $E'/E'_{PC} = 2.36/2.04$ (GPa/GPa) and 2.70/2.04 at 30°C, for example, or an increased stiffness up to 0.66 GPa or 30%. We estimated the effective Young’s elastic modulus of the component graphene layers as 360 GPa with the rule of mixtures, agreeing with reported values of 210 to 510 GPa for CVDG with ripples (3, 14). Uniaxial tension (fig. S10) and microindentation results (fig. S11) demonstrate similar elastic modulus increase with a linear dependence on $V_{G}$. For comparison, a minimum of $2\% < V_{G} < 5\%$, 10 times more than $4^j$ composites, is required to achieve comparable stiffness of PC nanocomposites in the limit of 3D random orientation for graphene oxide (GO) or derivatives with typical aspect ratios $a = 20$ to 50 (15–18) (Fig. 3C). Nanoplatelets with smaller $a$ values contribute less to reinforcement (fig. S12; GOx (or derivatives)
with multilayer structures generally have poor interlayer bonding (19, 20), which further minimizes the reinforcement. The atomic thinness of monolayer CVDG and its near-infinite a maximize this reinforcement (Fig. 3C).

We also verified that the PC matrix of our composite is not itself stiffening, evidenced by the reduction of the glass transition temperature (T_g) from 151.3° to 141.8°C at higher V_G (fig. S13) and no detectable increase in crystallinity of the PC (Fig. 3A). The reinforcement then comes from the direct load transfer to graphene filler itself (21), distinguishing it from cases where the inclusion (e.g., GO) stiffens the polymer matrix and increases

\[ T_g \] by restricting polymer-chain mobility near the polymer-inclusion interface (19, 22) (fig. S14 and supplementary text 5). To date, we have demonstrated composites with V_G as high as 0.185%, but the 4j and shear scrolling methods allow one to reach as high as 2.5% (table S1), translating to \( \Delta E' \) or \( \Delta E'' \) = 9.0 to 20.6 GPa (Fig. 3C). Planar 4j samples at V_G = 0.185% also show higher \( E'' \) peak values (0.50 GPa) compared with those at V_G = 0.082% (0.40 GPa) and the PC control (0.26 GPa) (Fig. 3A). These samples possess an enhanced energy dissipation mechanism from in-plane translation and frictional sliding at the layer interfaces (fig. S10A) (23). Both \( E' \) and \( E'' \) increase with V_G, promising materials of stiffness and damping exceeding that of the matrix polymer at negligible increases in weight (24).

The spiral fibers also demonstrate interesting mechanical properties. Two Archimedean scroll fibers—fiber 1 (V_G = 0.185%) and fiber 2 (0.082%)—exhibit higher \( E' \) of 2.07 and 1.62 GPa, respectively, compared with PC controls at 1.14 GPa over 30° to 150°C (Fig. 3B). However, the stiffness of these scroll fiber composites was generally lower than that of the planar 4j composites. The scrolled structures of the fibers demonstrate a telescoping compliance mechanism (Fig. 3D, I) that involves internal axial rotation in addition to restricting polymer-chain mobility near the polymer-inclusion interface.
These fibers still exhibited measurable increases in stiffness \( \Delta E' \) of 0.38 and 0.93 GPa, however, and larger effective \( E'' \) of the CVDG at 500 GPa. This telescoping compliance necessarily reduced the diameter and densifying the structure uniformly (Fig. 3D, II, and fig. S15A). Axial rotation, in addition to translation, increases the path length per unit axial strain, hence increasing the \( E'' \) and energy dissipation through interfacial friction, increasing at higher \( V_G \) (Fig. 3B).

These fibers also show an extraordinary elongation at break (\( \varepsilon_{\text{max, break}} \)) up to 1.10 (Fig. 3E and fig. S15, B to E), compared with \( \varepsilon_{\text{max}} = 0.75 \) for a monolithic PC film (fig. S15F) (25) and higher ultimate strengths of 160 MPa (fiber 1) and 135 MPa (fiber 2), compared with 120 MPa for the PC films (fig. S15F) and fiber (Figs. 3E) (26). For an Archimedean spiral described by radius \( r \), the cross section follows \( r = a \theta \), with \( a \) the interlayer distance between successive turnings through the angle \( \theta \). The scroll fiber is unique,
where \( S_0 \) is identically the starting width of the graphene sheet (2.2 cm). For a fiber of diameter 131 ± 3 \( \mu \)m, as in Fig. 10, Eq. 3 predicts a \( t \) of 390 ± 20 nm, in agreement with ellipsometer measurement values of 390 ± 4 nm (table S1). The scroll architecture mandates that all of \( m = S_0 / b_{cc} \) (where \( b_{cc} \) is the carbon-carbon bond length, \( 0.142 \) nm) carbon-carbon bonds in the graphene rupture for complete failure or collapse, a process that takes place over a large strain range due to the semi-infinite nature of the graphene herein.

This can be seen in the images of the break sites with visible spiral ripping in III to V of Fig. 3D. The semi-infinite nature of the graphene herein.

**REFERENCES AND NOTES**

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**SUPPLEMENTARY MATERIALS**

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Materials and Methods

Supplementary Text

Figs. S1 to S18

Table S1

References (30–59)

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Stacking up the filler material
In composite materials, a strong or stiff filler is added to a softer matrix to create a combined material with better mechanical or electrical properties. To minimize the filler content, it needs to be uniformly distributed in the composite, which is particularly challenging for nanoscale materials. Liu et al. alternately stacked sheets of graphene and polycarbonate to make a base composite. By further cutting and stacking, up to 320 aligned layers were made with a very uniform filler distribution. Alternatively, the initial stack could be rolled into a rod. In both cases, the properties exceeded what might be expected from a simple combination of the two materials. Science, this issue p. 364

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