



## Regular article

# Leaf-like carbon nanotube-graphene nanoribbon hybrid reinforcements for enhanced load transfer in copper matrix composites



Ming Yang<sup>a</sup>, Lin Weng<sup>a</sup>, Hanxing Zhu<sup>b</sup>, Fan Zhang<sup>a</sup>, Tongxiang Fan<sup>a,\*</sup>, Di Zhang<sup>a</sup>

<sup>a</sup> State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China

<sup>b</sup> School of Engineering, Cardiff University, Cardiff CF24 3AA, UK

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## ABSTRACT

A leaf-inspired nanoengineering is employed for the structural design of carbon nanofillers. We fabricate leaf-like carbon nanotube (CNT)-graphene nanoribbon (GNR) hybrids as novel reinforcements for a copper matrix composite. The straight and stiff CNT 'midribs' are conducive to individual dispersion whilst the two-dimensional GNR 'margins' provide more sufficient interface contact area and deformation gradient zone, giving rise to significantly improved interfacial load transfer and mechanical strength as compared to the unmodified nanotubes. The mechanics and strengthening mechanisms are further rationalized by finite element analysis and the generalized shear-lag theory.

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Carbon nanotubes (CNTs) have attracted considerable attention as composite enhancers in the past two decades, owing to their extraordinary one-dimensional (1D) sp<sup>2</sup>-bonding nanostructure and fascinating physico-chemical properties. Specifically, despite constant progress in the field of CNT-reinforced metal matrix composites (MMCs), the reinforcing efficiency is still notably lower than the theoretically predicted result [1,2]. This has been attributed to the agglomeration and non-uniform dispersion of CNTs, the poor cohesion strength and negligible load-transfer at the metal-inorganic interface, as well as the damage of CNTs during processing. In this regard, various kinds of techniques, including friction stir processing [3], high energy ball milling [4], in-situ grown [5], flake powder metallurgy [6–8], solution mixing [9], molecular level mixing [10], interfacial modification [11] and so forth, have been developed to address the CNT aggregation and improve the interfacial conditions between CNT and metals. However, little attention has been paid to investigating the effect of structural modification of multi-walled CNTs (MWCNTs), and the ensuing interfacial and mechanical responses still remain unclear.

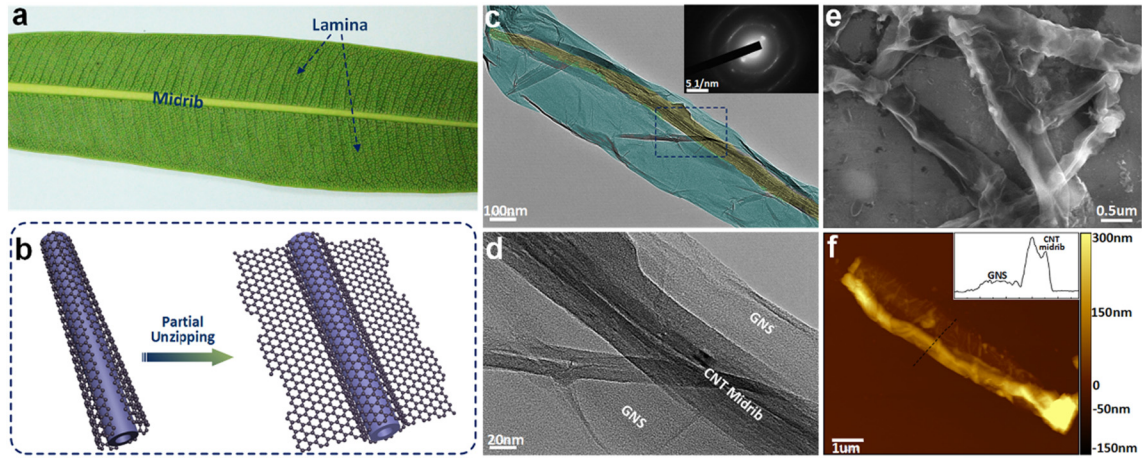
Notably, when serving as nanofillers, their size, dimension and geometry substantially dictate the interfacial configuration, load-transfer characteristic and consequently the overall mechanical performance of composites at the macroscale [12,13]. For example, Alivisatos et al. [14] have reported that branched nanofillers have the potential for optimization of nanocomposite Young's modulus over their linear counterparts. In the case of CNT-reinforced MMCs, because of poor

mechanical interlocking and easy interfacial sliding between nanotubes and the matrix, the dominant failure mechanism is usually attributed to the pull-out mode, significantly limiting the reinforcement role [8,15,16]. In addition, exceptional strength of nested inner graphene cylinders in MWCNTs is barely exploited, because the extremely weak inter-wall shear resistance allows only the defective outermost walls to carry the load [17]. In fact, MWCNTs are inherently composed of nested and curled graphene layers. Therefore, it is feasible to in-situ fabricate inter-connected CNT-graphene hybrids, which is promising to benefit the metal-nanocarbon interfacial shearing and a full exert of the load-bearing ability of CNT walls.

Plant leaves, typically consisting of a robust midrib and planar leaf laminae (Fig. 1a), are elegantly evolved to be strong enough to suffer from external damages owing to their structural coupling effect. Inspired by the configuration of plant leaves, here we report a structural design of carbon nanofillers, in which the middle nanotube and the graphene nanoribbon (GNR) wings are cross-linked by carbon sp<sup>2</sup>-bonding, for synergistically enhancing the load-transfer efficiency and mechanical properties of MMCs. Mass leaf-like CNT-GNR hybrids (denoted as LCGHs) are synthesized through well-controlled unzipping of the outermost layers of MWCNTs. Herein, the inherent CNT midrib serve as a strong and stiff framework to avoid GNR coagulation, whilst the exfoliated GNR parts provide high surface area and abundant hydrophilic oxygenated groups that can introduce more robust interfaces for carrying load as well as facilitating their dispersion in solvents. We achieve an substantial enhancement of load-transfer efficiency and the ensuing boost of mechanical strength in copper matrix composites infused with individually embedded LCGHs (designed as Cu/LCGHs) as

\* Corresponding author.

E-mail address: [txfan@sjtu.edu.cn](mailto:txfan@sjtu.edu.cn) (T. Fan).



**Fig. 1.** (a) Photograph of *Nerium indicum* Mill. leaves showing typical midrib-margin structure. (b) Schematic representation of the development of LCGHs inspired by leaf structure. (c–d) TEM and HR-TEM images of LCGHs, inset is the corresponding SAED pattern. (e) SEM image of LCGHs. (f) AFM topography of a single LCGH, inset is the corresponding height profile.

compared to those reinforced with unmodified CNTs (**Cu/UCNTs**), which highlights the effect of this customization of carbon nanostructure. The mechanics and strengthening mechanisms are further rationalized by finite element analysis and the generalized shear-lag theory, which suggest that the strong interfacial bonding, optimized orientation control and especially the unique geometric factors of the novel hybrid reinforcement are conducive to a more effective capability for transmitting stress from Cu matrix.

Bulk LCGHs were firstly prepared by mimicking the typical midrib-margin structure of *Nerium indicum* Mill. leaves (Fig. 1a) through chemical unzipping of several outer-layers of MWCNTs by the conventional Hummers method [18], as illustrated by the schematic showing of Fig. 1b. Herein, the few-layered GNRs, exfoliated from the MWCNTs and extended seamlessly from the perimeter of an individual CNT, are like leaf laminae, whilst the intact nanotube is similar to a leaf midrib. This configuration change is unambiguously proved by transmission electron microscope (**TEM**, JEM-2100F, JEOL) images (Fig. 1c–d), scanning electron microscope (**SEM**, S-4800, Hitachi) image (Fig. 1e) as well as the atomic force microscope (**AFM**, MultiMode-8, Bruker) topography (Fig. 1f). The well-defined selected area electron diffraction (**SAED**) pattern (Fig. 1c inset) shows elongated diffraction rings along the tube axis, which suggests a retention of crystalline structure and inherent nanotube of LCGHs [19]. Moreover, AFM height profile (Fig. 1f inset) also demonstrates a CNT core of ~100 nm thick coupling with side GNR wings of several nanometers thick (<10 layers).

A wet-fusing assembly approach (namely, the hetero-aggregation method [9,12]), which enables quick assembly, clean interface and scalable preparation, was adopted to obtain homogeneously mixed copper-nanofiller hybrid powders. LCGHs are well-dispersed in solvents because they are enriched with negatively charged, hydrophilic moieties (carboxyl, hydroxyl and epoxy groups) after chemical oxidation, as verified by X-ray photoelectron spectroscopy (**XPS**, AXIS UltraDLD, Kratos) profile (Fig. 2a) and Fourier transform infrared (**FTIR**, Nicolet 6700, ThermoFisher) spectra (Fig. S1) [19]. The stiff and straight midribs are also conducive to the dispersion of individual LCGHs, because the GNR parts are prone to aggregate due to strong van der Waals interactions and the large surface area [18]. Concurrently, Cu powders with an average diameter of 0.2–2 μm have positive charge on the surface when dispersed in ethanol solution [9]. As a result, when the two suspensions are co-blended, a large number of Cu powders are available to arrest, sandwich and anchor individual LCGHs through electrostatic force adsorption, giving rise to well-dispersed LCGHs inside the co-deposits (Fig. 2b). The hybrid powders were easily collected and then consolidated and transformed into a fully dense, macroscopic bulk by spark plasma sintering (**SPS**) and large-strain hot rolling ( $\epsilon = 1.97$ ). Meanwhile, lengthwise rotation of LCGHs occurred in the copper matrix during

these heavy co-deformations, which otherwise induces LCGH realigning along the rolling direction (**RD**), as shown in Fig. 2c. Cu/UCNTs that have almost identical microstructure with Cu/LCGHs were also prepared as reference materials, using the same processing conditions, and the details of the fabrication procedure, material characterization and test are provided in the supplementary material.

Mechanical strength data of Cu/LCGHs, Cu/UCNTs and unreinforced Cu matrix obtained from tensile tests are summarized in Figs. 2d, S2 and Table S1. Cu/LCGHs clearly outperform Cu/UCNTs for improving the tensile strength of Cu matrix (an increase of 39.1–130% and 31.0–97.3%, respectively). The strength of MMCs has been described on the basis of a simplified shear-lag model, according to which the applied load is transferred to carbon nanofillers through shear stress developed in the compliant metal matrix [7,15]:

$$\sigma_c = \alpha V_f \sigma_f + (1 - V_f) \sigma_m$$

$$\text{For } s > s_c, \alpha = 1 - \frac{\sigma_f}{\tau_m s}; \text{ For } s < s_c, \alpha = \frac{\tau_m s}{\sigma_f}$$

where  $\sigma_f$ ,  $V_f$ ,  $s$  are the tensile strength, volume fraction and aspect ratio of the reinforcement, respectively;  $\tau_m$  is the matrix shear yield strength (58 MPa),  $s_c$  is the critical aspect ratio given by  $s_c = \frac{\sigma_f}{2\tau_m} = 86.2$ . A comparison of the relative strength of composite to matrix ( $\sigma_f/\sigma_m$ ) with those expected from the shear-lag model demonstrates that the strength data of Cu/UCNTs agree well with the theoretical predictions, whilst the  $\sigma_f/\sigma_m$  values of Cu/LCGHs are well above the predicted curve. This verifies the conjecture that the leaf-like nanofillers are substantially more distinguished than pristine CNTs for reinforcing metals.

The superior strengthening capability is further illustrated by isolating the load-bearing effects of LCGHs and UCNTs. The strength increment of nanocarbon reinforced MMCs is generally ascribed to a synergy of Hall-Petch strengthening ( $\Delta\sigma_{H-P}$ ), load-transfer effect ( $\Delta\sigma_{L-T}$ ), geometrically necessary dislocation strengthening ( $\Delta\sigma_{GND}$ ), and Orowan strengthening ( $\Delta\sigma_{Orowan}$ ) [12,16,20]. In detail,  $\Delta\sigma_{H-P} = kD^{-1/2}$ , where  $k$  is a material constant and  $D$  the mean grain size;  $\Delta\sigma_{Orowan} = \frac{0.4MGb}{\pi\lambda(1-\nu)^{1/2}} \ln\left(\frac{\pi\gamma_s}{4b}\right)$ , where Taylor factor  $M = 3.06$ , shear modulus  $G = 42.1$  GPa, Poisson's ratio  $\nu = 0.355$ , Burgers vector  $b = 0.256$  nm, effective reinforcement particle diameter  $\gamma_s = \sqrt[3]{\frac{3d^2l}{16}}$ , and effective planar inter-particle spacing  $\lambda = \gamma_s(\sqrt{\frac{\pi}{4V_f}} - 1)$ ;  $\Delta\sigma_{GND} = \alpha Gb \sqrt{\frac{8V_f\epsilon_y}{b\gamma_s} + \frac{12V_f\Delta CTE\Delta T}{b(1-V_f)\gamma_s}}$ , where the constant  $\alpha = 1.25$ ,  $\epsilon_y$  is the yielding strain (0.2%),  $\Delta CTE$  is the coefficient of thermal expansion (**CTE**) mismatch between nanocarbon and Cu, and  $\Delta T$  is the maximum temperature change during thermomechanical processing;  $\Delta\sigma_{L-T}$  is equal to

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