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Novel Multifunctional Hierarchical Composite Aerostructures with Enhanced Fracture Toughness and Bulk Conductivity

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The work is focused on the development of novel nano-engineered hierarchical carbon fibre reinforced polymer (CFRP) composites with increased through-thickness fracture toughness and electrical conductivity, while preserving the in-plane mechanical properties. The strategy that was explored involved the growth of graphene nanoflakes (GNFs) directly on carbon fibers in a radial fashion.

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Novel Multifunctional Hierarchical Composite Aerostructures with Enhanced Fracture Toughness and Bulk Conductivity, Utilizing Graphene Nanoflakes Grown Directly on Carbon Fibres

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Final Technical report

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Award FA9550-17-1-0042

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Interlaminar fracture toughness of GNF nano-enhanced CF composites was assessed by Mode I, II interlaminar fracture toughness tests. Specimens incorporating GNFs grown directly on CFs by radio-frequency–plasma enhanced chemical vapour deposition (rf-PECVD) method exhibited clear increase in fracture toughness compared to bare counterparts. The tensile strength tests showed that under specific growth conditions the composites' strength can be maintained.

Moreover, in order to compare the grown hierarchical structures with ones originating from other alternative methods, a novel and one-step CO_2 laser texturing process of CFs was examined as well. The results of the CO_2 irradiation of the CF fabrics, showed that this method can be considered as a quick and low-cost technique for producing composites with boosted out of plane electrical conductivity, without negatively affecting the interlaminar region of them (preservation of the Mode-I interlaminar fracture toughness).

Furthermore, substantial effort has also been devoted in demonstrating the application of GNFs in structural energy storage. We fabricated structural supercapacitor devices by utilizing directly grown graphene nanoflakes on carbon cloth as electrodes, glass fibres as separator and an ionic liquid-based polymer electrolyte (PEGDGE-IL) as structural and ion conductive matrix. Graphene nanoflakes were grown on as purchased carbon fibres by one step radio-frequency–plasma enhanced chemical vapour deposition (rf-PECVD) method. The GNF modification of the CFs produced a 10 fold improvement in the specific capacitance of bare fibres, whereas further activation of the CF/GNFs cloth with urea led to a 20 fold improvement.

All-in-all the work has resulted in 4 journal papers completely or partly funded by this AFOSR/EOARD grant. Some of the work has been done in collaboration with University of Ioannina, Greece) with Prof. Alkis Paipetis and his team.

The Team

This project was run by an interdisciplinary team at Ulster University headed by Prof. Papakonstantinou. A number of researchers and technical staff were involved in the execution of the project, however the major part was conducted by one Ph.D. student and one post-doc.

PI: Prof. Pagona Papakonstantinou

Key Researcher: Dr Abhijit Ganguly

PhD Student: Dr Anastasios Karakassides

Dr Abhijit Ganguly

Dr Anastasios Karakassides

Prof. Pagona Papakonstantinou

Highlights

Highlights among the accomplishments of the Ulster's team in the EOARD project "Novel Multifunctional Hierarchical Composite Aerostructures with Enhanced Fracture Toughness and Bulk Conductivity, Utilizing Graphene Nanoflakes Grown Directly on Carbon Fibres":

- Radially aligned graphene nanoflakes (GNFs) grown on carbon fibres (CFs) were used as an interface to increase the interfacial strength and conductivity of CFRP composites.
- GNFs provided embedded functionality via increased electrical conductivity and electrochemical capacitance.
- Direct growth of graphene nanoflakes (GNFs) on carbon fibres (CFs) led to improvement of interlaminar fracture toughness (Mode I & II) and tensile strength over bare CF composite counterparts.
- Structural supercapacitors utilising urea activation of GNF nano-enhanced carbon fibres displayed a >20 times improvement in specific capacitance over bare CF counterparts. This compares favourably over previous reported studies, which showed an improvement of no more than 8-fold.
- There is a strong dependence of strength and toughness on the surface morphology of GNFs in CFRPs.
- The results of this work demonstrated the unique potential of GNFs, as an excellent nano-reinforcement and electrically conducting interface, for achieving simultaneously strong, tough, and conducting multifunctional CFRP composites.

- Results on laminates comprised of CO_2 irradiated unidirectional CF cloths, demonstrated an enhancement in out of plane electrical conductivity, while preserved the Mode-I interlaminar fracture toughness of the composites.

Papers published in peer-reviewed journals with EOARD/AFOSR funding

Anastasios Karakassides, Abhijit Ganguly, Kyriaki Tsirka, Alkiviadis S. Paipetis, and Pagona Papakonstantinou. Radially Grown Graphene Nanoflakes on Carbon Fibers as Reinforcing Interface for Polymer Composites. *ACS Applied Nano Materials* **2020**, 3, 2402-2413. https://doi.org/10.1021/acsanm.9b02536

The development of nanoscale reinforcements, which can tailor the interfacial strength and impart multiple functionalities on carbon fibre reinforced polymer (CFRP) composites, remains a challenge for their large-scale adoption in diverse applications ranging from aerospace to transportation and construction industries. In this work radially aligned graphene nanoflakes (GNFs), grown directly on carbon fibres (CFs) via a simple one-step microwave plasma enhanced chemical vapour deposition method, without any catalyst, were used as a novel nano-reinforcement interface. A remarkable 28% enhancement in the tensile strength of the hybrid fibres was observed via single-fiber tensile strength tests, whereas the interfacial shear strength (IFSS) increased by 101.5%. Our results demonstrate that GNFs not only improve the interfacial strength between the GNFs and the epoxy resin but also enhance the in-plane mechanical strength of the CFs—a well-known problem encountered with the direct growth of carbon nanotubes on CFs. In addition, GNFs provided embedded functionality via increased electrical conductivity (60.5% improvement for yarns and 16% for single fibre) and electrochemical capacitance (157% for yarns). This work indicates the potential of GNFs as an interphase for the simplified and cost-effective production of stronger multifunctional CFRP composite materials.

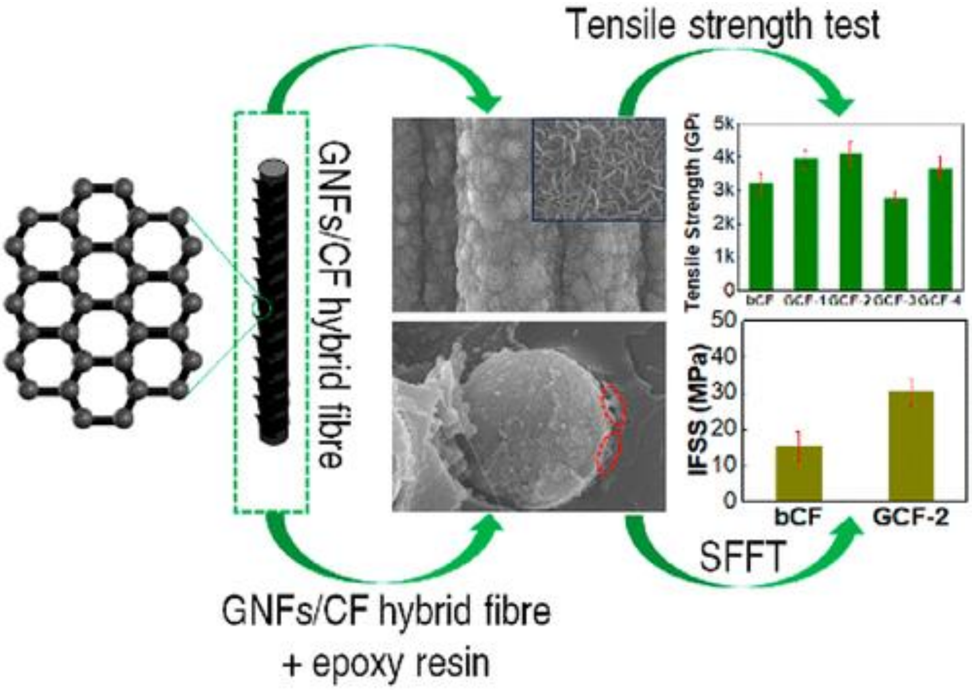

Figure 1. Schematic illustration of GNFs/CF hybrids and representative results of the tested samples.

Abhijit Ganguly, Anastasios Karakassides, John Benson, Shahzad Hussain, and Pagona Papakonstantinou. Multifunctional Structural Supercapacitor Based on Urea-Activated Graphene Nanoflakes Directly Grown on Carbon Fiber Electrodes. *ACS Applied Energy Materials* **2020**, 3, 4245–4254. https://doi.org/10.1021/acsaem.9b02469

Structural energy storage systems offer both load bearing and electrochemical energy storage capabilities in a single multifunctional platform. They are emerging technologies for modern air and ground transportation vehicles, promising considerable mass and volume savings over traditional systems. To this end, carbon fibre reinforced composites have attracted interest for structural supercapacitors (SS), emanating principally from their similar laminate design. However, carbon fibre (CF) electrodes suffer from poor electrochemical storage performance. To tackle this deficiency, carbon fibre electrodes were modified with a 3D network of radially grown graphene nanoflakes (GNFs) to enhance their degree of graphitization and active surface area. We show that the GNF surface morphology offers an ~ 9 times increase in specific capacitance (C_{sp}) of CF structural supercapacitor. Moreover, chemical activation of the GNFs/CF hybrid electrodes by urea induces a further improvement in C_{sp} by ~ 14 times, while almost maintaining the elastic modulus of the control CF-based device. It has been established that the high specific capacitance stems from the highly electroactive edge-dominated nitrogen moieties and enhanced electrical conductivity induced by urea activation. Overall, the urea-activated hybrid electrodes offer an ~ 12-fold increase in energy and power densities compared to CF control structural supercapacitor devices. These findings provide important knowledge for the design of next-generation multifunctional energy storage electrodes by highlighting the importance of interfacial nanoengineering.

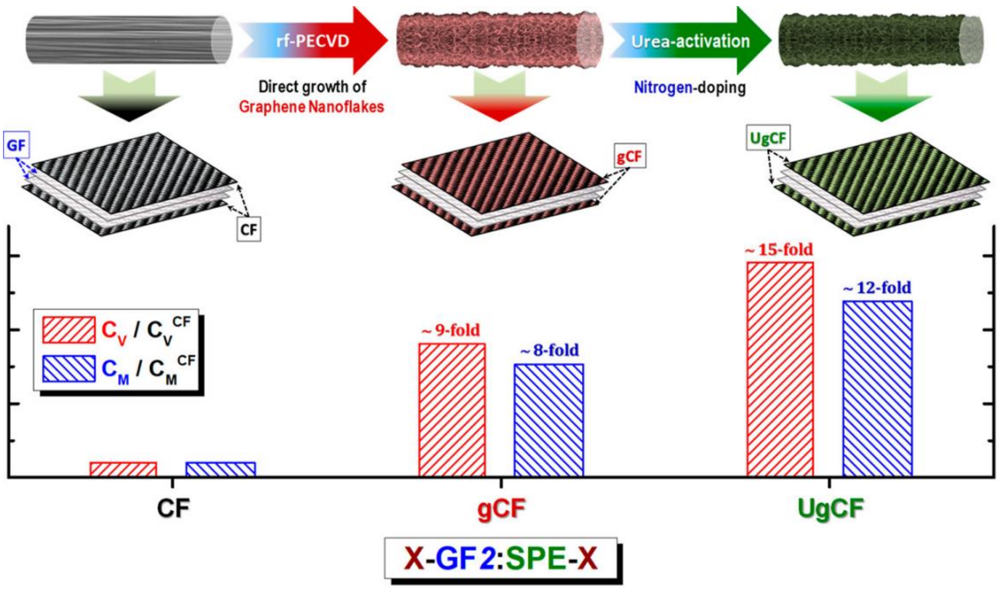

Figure 2. Schematic illustration of SS fabrication and representative results.

Anastasios Karakassides, Angeliki Karakassides, Michaella Konstantinidou, Alkiviadis S. Paipetis, and Pagona Papakonstantinou. Enhanced out of Plane Electrical Conductivity in Polymer Composites Induced by CO_2 Laser Irradiation of Carbon Fibers. *Applied Sciences* **2020**, 10, 356. https://doi.org/10.3390/app10103561

The creation of a hierarchical interface between the carbon fibre (CF) and the epoxy resin matrix of fibre-reinforced polymer (CFRP) composites has become an effective strategy for introducing multifunctional properties. Although the efficacy of many hierarchical interfaces has been established in lab-scale, their production is not amenable to high-volume, continuous, cost effective fibre production, which is required for the large-scale commercialization of composites. This work investigates the use of commercially available CO_2 laser as a means of nano-structuring the surface of carbon fibre (CF) tows in an incessant throughput procedure. Even though the single carbon fibre tensile strength measurements showed a decrease up to 68% for the exposed CFs, the electrical conductivity exhibited an increment up to 18.4%. Furthermore, results on laminates comprised of irradiated unidirectional CF cloth, demonstrated an enhancement in out of plane electrical conductivity up to 43%, while preserved the Mode-I interlaminar fracture toughness of the composite, showing the potential for multifunctionality.

This work indicates that the laser-induced graphitization of the CF surface can act as an interface for fast and cost-effective manufacturing of multifunctional CFRP composite materials.

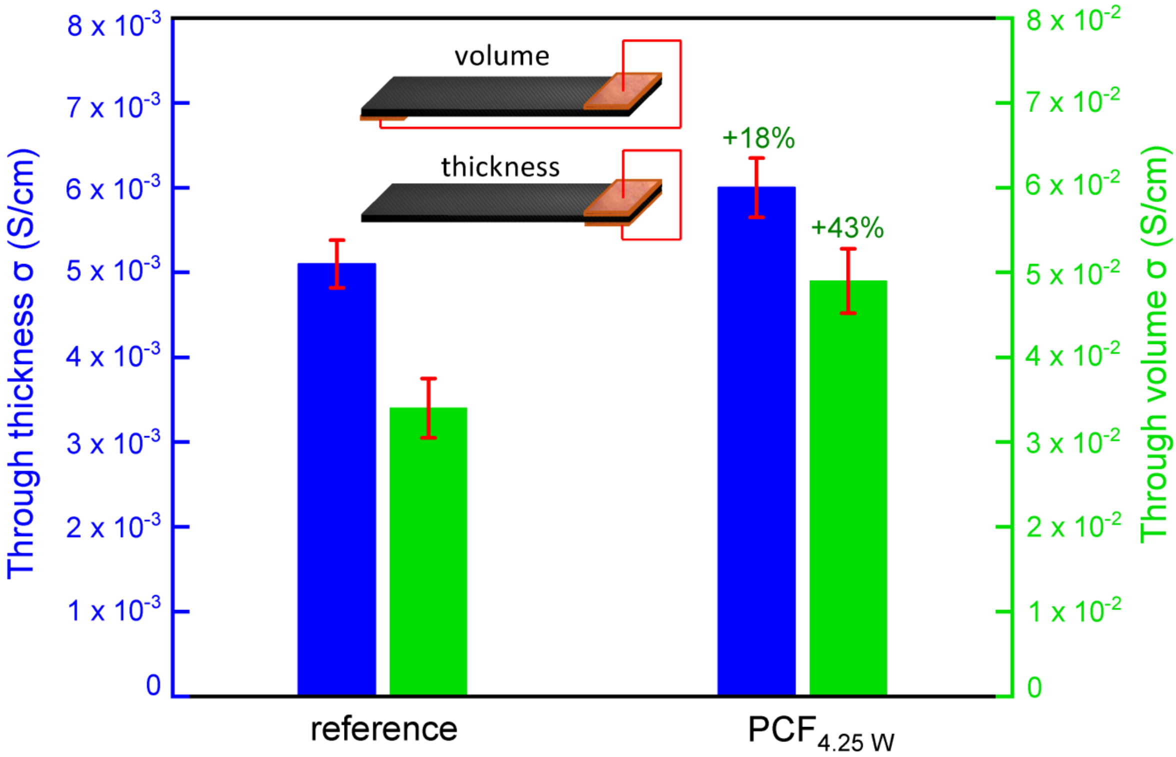

Figure 3. Out of plane electrical conductivity (σ) of the fabricated composite structures.

Anastasios Karakassides, Abhijit Ganguly, John Kelly, Preetam K. Sharma, and Pagona Papakonstantinou. Radially Grown Graphene Nanoflakes for Tough and Strong Carbon Fiber Epoxy Composites. *ACS Applied Nano Materials* **2021, 4, 9167-9180.** https://doi.org/10.1021/acsanm.1c01722

A long-standing challenge in structural material design is the simultaneous attainment of high strength and toughness, a conflicting requirement rarely met in engineering materials, with important technological applications in aerospace, defense, automobile, and marine industries. Motivated from examples in biological materials, to address this challenge, we demonstrate that strong and damage-tolerant carbon-fibre-reinforced polymers (CFRPs) can be realized via the direct growth of self-assembled radially aligned graphene nanoflakes (GNFs) on carbon fibres (CFs). Here, we report a first-of-its-kind study on the dependence of strength and toughness on the surface morphology of GNFs in CFRPs. The results indicated that fracture toughness was dependent on the density and waviness of the GNFs, whereas the tensile strength was also affected by the periodicity of the coated carbon fibre layers into the laminated structures. Notably, GNFs with reduced waviness and increased number of layers exhibited enhancement in interlaminar fracture toughness for modes I and II by 93.8% and 43.3%, respectively, whereas GNFs with increased waviness led to a marginal increase or preserved tensile strength. The highly interconnected and wavy nature of GNFs facilitated effective load transfer in both in-plane and out-of-plane directions. Moreover, the out-of-plane through-volume conductivity was remarkably enhanced by 527%. The results of this work demonstrated for the first time the unique potential of GNFs, as an excellent nanoreinforcement and electrically conducting interface, for achieving simultaneously strong, tough, and conducting multifunctional CFRP composites.

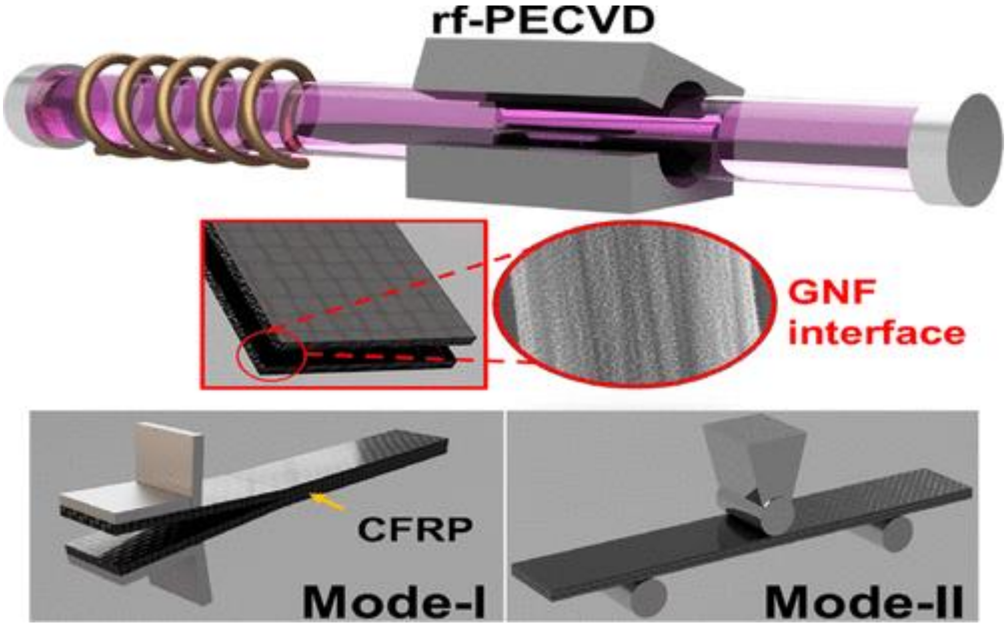

Figure 4. Schematic illustration of the GNF growth and mechanical characterization of the fabricated composites throughout interlaminar fracture toughness tests.