THE USE OF 3D GRAPHENE NETWORKS FOR THE CREATION OF BIO-INSPIRED SELF-MONITORING TOUGH CERAMIC NANOCOMPOSITES

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Over the years, material scientists have been increasingly looking at the design of natural structural composites such as bone or nacre in search of bioinspired design concepts \[1\]. Natural materials are typically based on very simple components with their unique properties often coming from complex architectures rather than materials. They usually exhibit complex anisotropic architectures over many hierarchical length scales, with either platelet or fibrous reinforcements \[2\]. Furthermore, to a large extent their mechanical properties - in particular toughness - depends on the careful engineering of interfaces. These design concepts have also been employed in synthetic composites and, in particular, weak interfaces are often used in ceramic-based materials as a way to promote toughness through mechanisms such as crack deflection and fibre or platelet pull-out \[3\]. On top of unique mechanical characteristics such as a combined high stiffness and toughness, natural materials also exhibit a number of multi-functionalities such as (damage) sensing and self-repair.

Here graphene opens new opportunities as its 2D structure is very well adapted to interfacial engineering as well as adding other functionalities. One of the critical features of some natural systems that has been very difficult to replicate synthetically is the presence of very thin (few nanometres) weak interfaces separating hard, mineral layers. In this study we take advantage of the 2D nature of graphene to engineer a fine network of internal weak interfaces in a brittle glass ceramic matrix. We use networks of chemically modified graphene as the starting point to create composites with layered architectures and an interconnected carbon network. The use of graphene allows the engineering of very thin (< 20 nm) nano-rough, interfaces. Despite the fact that the matrix is brittle and constitutes \textasciitilde 99 vol.% of the composite material, these interfaces promote stable crack growth and a fracture resistance up to an order of magnitude (in terms of energy) higher than that of the glass ceramic. In addition, they also provide a highly electrically conductive network (conductivity > 500 S/m) that can be used to sense the formation and progress of damage. This combination of self-monitoring and high-fracture resistance can help to create intelligent composite materials able to avoid catastrophic failure in service and illustrate a different approach for the integration of graphene in ceramic and polymer-based composites as opposed to traditional ‘reinforcement’ strategies.

Graphene networks were made by freeze casting. For this graphene oxide (GO) suspensions in water were prepared through the chemical exfoliation of large graphite flakes. These suspensions were frozen directionally to form 3D porous networks with macroscopic dimensions and a characteristic anisotropic layered architecture templated by ice. The internal structure of the network consists of long microscopic channels oriented along the ice growth direction (Figure 1a).
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Subsequently, the networks were freeze dried and heat treated at 900 °C in a reducing atmosphere to form reduced graphene oxide (rGO). After treatment, the network walls are extensively wrinkled (Figure 1b) due, in part, to a ~20 vol.% shrinkage induced by the carbonization process, which contributes to an effective restoration of the sp2 carbon network. These 3D porous graphene networks were subsequently infiltrated with polymethyl siloxane, a pre-ceramic polymer which was chosen for its high ceramic yield (90%), and heat treated up to 1000 °C in N2 to convert the siloxane polymer to a silicon oxycarbide glass (Si-O-C). In order to increase the density of the composite and further restore the sp2 network of the rGO, the samples were sintered by Spark Plasma (SPS).

The carbon network modifies the fracture behaviour of the matrix. The reduced graphene has formed a continuous network of weak interfaces that promote microcracking, crack branching and deflection, and an increase in fracture resistance of up to an order of magnitude (in terms of energy) than that of the pure glass ceramic (Figure 1c). In addition, the continuous graphene interfaces provide a highly interconnected conductive network at a low graphene content of 1 vol.% that can act as an efficient Joule heater (with a potential application in self-healing) or can be used to monitor the formation of defects and crack propagation (Figure 1d).

Figure 1. (a) Freeze dried 3D porous graphene network with a characteristic anisotropic layered architecture by ice-templating. (b) A dense Si-O-C nanocomposite is obtained after infiltration with pre-ceramic polymer and pyrolysis. (c) While the glass-ceramic is brittle, the composite exhibits stable crack-propagation (insert shows typical force-displacement curve with the arrow indicating crack initiation) with a rising resistance curve (R-curve). (d) The finely interconnected network leads to electrical conductivities that are one to two orders of magnitude higher than for other ceramic nanocomposites with similar contents of carbon nanofillers.
A very interesting aspect of the current approach is that graphene is not used as a conventional “nano-reinforcement” but rather as a means to engineer a fine network of weak interfaces that provide electrical conductivity and fracture resistance to brittle matrices. Hence, using a property graphite has been well known for, namely that of a dry lubricant. These results underline the need to look at alternative approaches in the way we design and build practical composite materials using nanomaterials and that these approaches will need to integrate mechanical and functional response.

REFERENCES


