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Graphene-reinforced silicon oxycarbide composites prepared by phase transfer

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ABSTRACT

In order to compensate for cracking, brittleness and low electrical conductivity of polymer-derived silicon oxycarbide (SiOC), graphene was successfully introduced into a SiOC matrix by phase transfer of graphene oxide (GO) from an aqueous (GO dispersed in water) to organic phase (copolymer as SiOC precursor in diethyl ether). Spark plasma sintering (SPS) was used to fully densify composites to ~2.3g/cm^3. The prepared materials were comprehensively characterized and exhibited significant enhancement in the mechanical properties, electrical conductivity and electrochemical performance. Self-assembled lamellar structure of graphene in the SiOC-matrix was achieved, leading to anisotropy in the properties of the composites. The fracture toughness of the SiOC-2vol%GO composite was increased by ~91%, at the expense of a slight decrease in the flexural strength, compared to the SiOC-matrix. Moreover, the composites exhibited three orders higher electrical conductivity than the SiOC-matrix. The electrical conductivity in the perpendicular direction ($\sigma_\perp = 3 \times 10^{-1}$ S/cm) of SiOC-2vol%GO composites was two orders of magnitude higher than that in the parallel direction ($\sigma_\parallel = 4.7 \times 10^{-3}$ S/cm), owing to the self-assembled lamellar graphene in the SiOC-matrix. The SiOC-2vol%GO composites further showed better electrochemical performance of oxygen reduction reaction (ORR) than pure graphene, exhibiting an onset potential (~0.75 V vs RHE) and more positive half-wave potential (~0.6 V vs RHE).

1. Introduction

Polymer derived ceramics (PDCs) have attracted great attention during the past 40 years, mainly for producing silicon-based advanced ceramics [1]. Silicon oxycarbide (SiOC) shows excellent thermal resistance due to the incorporation of carbon element into the silica system, containing SiO_2 and SiC rich phases [2,3]. SiOC is one of the most commonly-used polymer-derived ceramics and can be generally produced from curing (crosslinking) and pyrolyzing ceramic precursors (eg. vinylester resins, siloxanes) [4–6]. Polymer-derived SiOC is promising for electrochemical energy storage applications and micro-systems, owing to the disordered carbon phase and hybrid bonds of silicon with oxygen and carbon as well as excellent complex and near-net shape capability [7–9]. However, the application of polymer-derived SiOC has been significantly restricted, owing to the pores and cracks formed during the curing and pyrolysis process, its brittleness behaviour and low electrical conductivity ($\leq 10^{-3}$ S/cm). The introduction of a filler into the matrix contributed to an increased surface area, which provides the interfacial bonding to allow effective stress transfer, resulting in the improved mechanical properties of the composites [10–12]. Therefore, some fillers have been proposed to reinforce SiOC in the form of fibers [13] and ceramic nanoparticles [14]. High-temperature ($\geq 1000\,°C$) thermal treatment can contribute to the increased electrical conductivity (maximum: ~10^{-3} S/cm) of polymer-derived SiOC ceramic, owing to the formation of interconnected percolation networks of both crystalline SiC and carbon [15,16]. However, this requires the high-temperature stability of fillers, so most fillers can not compensate

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the drawback of SiOC in poor electrical conductivity. For example, the mechanical properties of the basalt reinforced SiOC composites were improved but they could not be heated above 1000 °C to achieve higher electrical conductivity, due to the significant softening of basalt fibres at high temperatures (≥1000 °C) [11,17].

The addition of graphene to polymer matrices has been intensively investigated due to its combination of excellent electronic, optical, thermal conductivity and mechanical properties [18,19]. Achieving well-dispersed graphene is widely accepted as a challenging issue, owing to its high surface area and hydrophobic nature [18,20]. Some techniques have been used to reduce the agglomeration tendency of graphene sheets, including ultrasonication dispersion [9,18] and ball milling [21]. However, the limitation of these methods is that they involve the process of mechanically mixing graphene and ceramic powders, thus being an inefficient method for polymer and polymer-derived ceramics. GO sheets have been proven to be an excellent alternative for producing graphene-ceramic composites, owing to their well-dispersion in water and industrial availability [22–25]. However, the ceramic precursors (eg. methyl-containing poly(siloxane) (PMS) and phenyl-containing poly(siloxane) (PPS)) are hydrophobic.

To solve the mismatch between the GO (hydrophilic) and ceramic precursors (hydrophobic), the GO sheets would need to be functionalized. Typically GO is functionalized under harsh conditions (i.e. high reaction temperature, strong reagents) [26,27]. Yuan et al. reported a way to avoid this, the GO sheets were functionalized by phase transfer of GO from an aqueous to an organic phase (the diblock copolymer) under ambient conditions via electrostatic attraction [28]. During this process, positively charged amine functions on the PAPMS segments in poly[dimethylsiloxane-co-(3-aminopropyl)methylsiloxane] (PDMS-3-PAPMS) electrostatically interact with the negatively charged carboxylic groups of the GO flakes. In our work, we seek to use Yuan et al.'s novel functionalization technique to produce a graphene-SiOC ceramic composite. This phase transfer technique can produce dispersions with high loadings (~4.8 wt%) of GO into SiOC preceramic polymers (eg. PMS, PDMS) despite the high viscosity of polymers. In our work, dense SiOC-GO composites were prepared by phase transfer and followed by high-temperature thermal treatment (up to 1700 °C) in SPS (Spark Plasma Sintering) device. The composite materials were comprehensively characterized and their mechanical properties, electrical conductivity, and electrochemical performance for oxygen reduction reaction (ORR) were investigated.

2. Experimental process

2.1. Processing of SiOC-GO composites

A copolymer solution was prepared by dissolving the copolymer poly[dimethylsiloxane-co-(3-aminopropyl)methylsiloxane] (PDMS-3-PAPMS, Sigma Aldrich) in the solvent, diethyl ether (GPR RECTAPUR®, VWR Chemicals, 99.9 wt%). The graphene oxide (GO) suspension (1 mg/mL) was prepared by diluting commercial graphene oxide (GO) water dispersion (4 mg/mL, Graphenea) with deionized water. Then the diluted GO suspension was injected into the prepared copolymer solution from the bottom of a glass container (Fig. 1). Due to the higher density of the GO suspension and its immiscibility with the copolymer solution, a biphasic mixture (Fig. 1) was formed. The upper transparent layer was the copolymer in diethyl ether and the bottom black layer was the GO suspension in water. The phase transfer was achieved by magnetically stirring the mixture for 24 h to speed the reaction between GO and copolymer at the biphasic (water/oil) interface (as shown in Fig. 1). 24 h was sufficient for all of the GO to diffuse into the diethyl ether, and this was clearly visible as the bottom layer became clear (absence of GO) and the upper layer became black with the functionalized GO@copolymer (weight ratio, m_{GO}: $m_{copolymer} = 1{:}10$). Pure GO@copolymer composite was obtained by draining the water phase and then drying the upper layer to remove the diethyl ether. The GO@copolymer was then redissolved in the solvent methyl isobutyl ketone (Sigma Aldrich, MIBK) using an ultrasonic bath to avoid agglomeration. This dispersion was then mixed with polymethylsiloxane (PMS, Silres® MK powder, Wacker Chemistry)

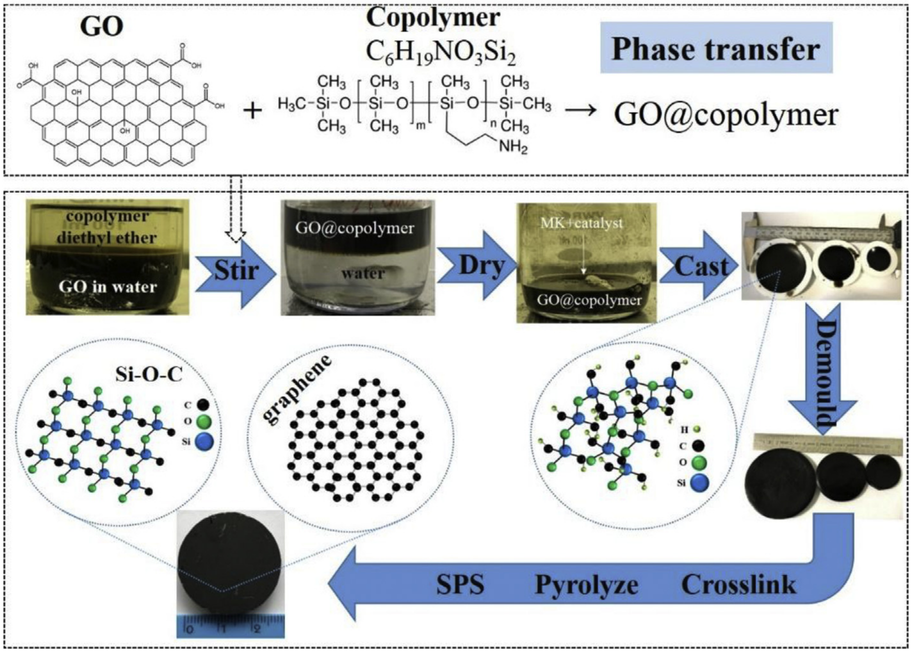

Fig. 1. Schematic illustration of processing SiOC-GO composites. (A colour version of this figure can be viewed online.)