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In-situ generation of graphene network in silicon carbide fibers: Role of iodine and carbon monoxide

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ABSTRACT

By iodine curing of polycarbosilane fibers followed by sintering under a controlled atmosphere of carbon monoxide, a unique strategy is developed for the *in situ* growth of graphene networks inside silicon carbide fibers. In the resulting fibers, three-dimensionally interconnected few-layered graphene sheets are well-dispersed in the nanocrystalline SiC, allowing for fast electron transport through the graphene networks. The roles of iodine and carbon monoxide in fabricating the graphene-network embedded SiC fibers are elucidated. The distinct evolution of graphene structure was observed in the iodine-treated Si(O)C using transmission electron microscopy and Raman spectroscopy. The iodine incorporated in the fibers induces the sp^2-hybridization of carbon, generating carbon–carbon double bonds and graphene seeds such as reduced graphene oxide, which are supposed to grow into graphene layers at elevated temperatures. Carbon monoxide is employed as a component of the atmospheric gas mixture during the decomposition of Si(O)C to suppress the evolution of SiO and CO gases, thereby restraining coarsening of SiC nanocrystallites and maintaining the integrity of the graphene network. These processes pave the way for designing graphene structures in polymer-derived ceramic materials for a broad range of applications.

1. Introduction

Silicon carbide (SiC) is an established high-temperature material owing to its strong polar covalent bond [1]. Since the development of polymer-derived SiC fibers by Yajima and co-workers [2,3], their application has been expanded; these fibers are not only used in ceramic matrix components (CMCs) in the aerospace [4,5] and nuclear fields [6–8], but also in membranes for polymer-electrolyte membrane fuel cells [9], thermal radiation heaters [10–12], and supercapacitor electrodes [13–15]. Accordingly, structural strength is no longer the only characteristic pursued for SiC fibers. The fibers will have broader application potential if they can acquire new functions along with high strength and flexibility.

If SiC fibers possess some degree of electrical conductivity, they may function as sensors for detecting structural changes throughout the fibrous networks along composites [16–19] or as electrical devices operating in extreme environments such as high voltages and temperatures, thanks to the high electron saturation velocity of SiC [19–22]. However, owing to the semiconducting nature of SiC, typical nanocrystalline SiC fibers have poor electrical conductivity, which limits their application [23].

The carbon phase (above the percolating level) in SiC fibers can be harnessed to endow the fibers with high electrical conductivity because of its intrinsically low electrical resistivity compared with that of the SiC phase. A conventional way to increase the conductivity is to use a precursor with high carbon content, thus leaving a sufficient amount of free carbon in the resultant fibers. Indeed, preceramic polymers with high carbon content have been utilized to develop carbon-rich silicon oxycarbide (Si(O)C)-based anodes for Li-ion batteries [24,25]. However, carbon should be carefully tailored for the fabrication of high-grade SiC fibers because the

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