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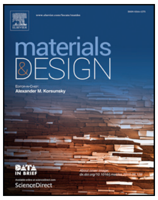

Synergistic effect on the mechanical behaviors of ternary graphene oxide-zirconium diboride-poly(vinyl alcohol) papers

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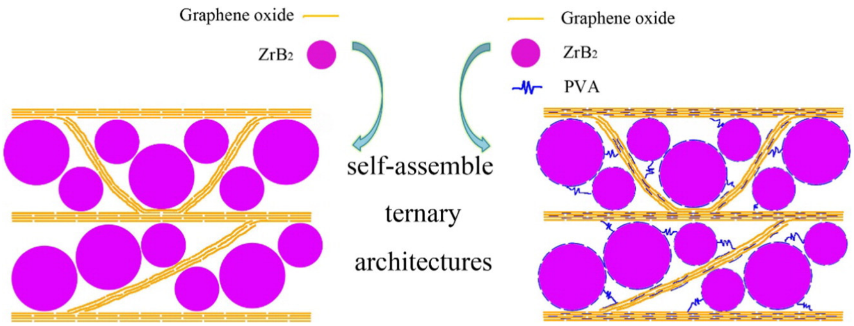
HIGHLIGHTS

- Ternary graphene oxide-zirconium diboride-poly(vinyl alcohol) microstructures are achieved during self-assembly process.
- Significant enhancements in tensile properties are achieved due to synergistic effect of graphene oxide-zirconium diboride-poly(vinyl alcohol).

GRAPHICAL ABSTRACT



Through design ternary graphene oxide structures and interlayer interaction between poly(vinyl alcohol), graphene oxide and zirconium diboride particles, significant enhancements in fracture strength (~200%) and tensile modulus (20–100%) are attained.

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ABSTRACT

Through design hierarchical architectures and interlayer interaction, multifunctional macroscopic graphene oxide papers tend to attain outstanding mechanical properties. Three dimensional architectures functionalized graphene oxide papers are self-assembled with zirconium diboride particles and poly(vinyl alcohol, PVA) using vacuum assisted filtration method. Firstly, ternary graphene oxide micro-scale structures are achieved by the addition of zirconium diboride particles. Then, PVA is introduced to enhance the interface interaction between graphene oxide nanosheets and zirconium diboride particles. The results show significant enhancements in fracture strength (~200%) and tensile modulus (20–100%) are attained through synergistic effect of ternary graphene oxide structures and interlayer interaction between PVA, graphene oxide and zirconium diboride particles.

1. Introduction

Owing to its remarkable mechanical properties and multifunction, such as excellent electrical, thermal and optical properties, two dimensional graphene has shown its potential application in electronics [1–3], energy storage and conversion [4,5], high temperature [6–8] and aerospace engineering [9,10]. The urgent quest in these practical applications is creating macro-scale materials using the nano-scale graphene. As one basic structural unit to build macroscopic graphene materials, graphene oxide (GO) is attracting more and more attention for its high yield, low cost and easily operation. GO is generally achieved by chemical oxidation-exfoliation of cheap graphite, the resultant oxygen-containing groups on the surface are easily modified by other functional groups. There are many techniques developed to fabricate macro-scale GO, such as ice templating [11], vacuum filtration [12], and liquid/air interface self-assembly [13]. Regardless of the method, the realization of functionalities of macroscopic GO materials should be ensured

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by their excellent mechanical properties which can be adjusted by designing microstructures of the hierarchical architectures.

Nature inspired GO paper with hierarchical architectures is one kind of important structural material among the macroscopic GO materials. However, the reported modulus and tensile strength of pure GO papers are generally in a relatively wide range of 1–42 GPa, and 80–150 MPa respectively, which are much lower than those of individual graphene sheets. The reasons mainly are the 'size dependent effect' and the inevitable stacked of GO sheets due to π-stacking and hydrophobic interactions in the self-assembly process [14]. To improve the mechanical properties of pure GO papers, an effective way is to build strong interfacial interaction between GO sheets [15], such as ionic bond [16], hydrogen bond [17] and covalent cross linking [18]. For example, Park et al. demonstrate that <1 wt% edge-bound Mg^{2+} or Ca^{2+} will result in 200% and 50% enhancement for stiffness and strength, respectively. When the load is acting on the modified GO paper, the edge-bound divalent ions bridging GO sheets can resist deformations to improve the mechanical properties. The covalent cross linking between the GO sheets and polymers, such as dopamine [19], poly(ether imide) [20] or 10,12-pentacosadiyn-1-ol [21], improves the fracture energy almost using the similar mechanisms as that of divalent ions. The advantage is that we can increase the length of the polymer chain between adjacent GO sheets to further improve the mechanical properties of GO paper. Another way to improve the mechanical properties is the introduction of bulk materials, such as MoS_2 sheets [22] or nanofibrillar cellulose [23], in the direction vertical to the plane of GO sheets to construct ternary structures. Then, more energy is needed to overcome the interaction of bulk materials in the axial direction and the slippage between hierarchical structures.

In this paper, we propose one simple method to construct macroscopic GO-PVA/ZrB_2 paper with novel three dimensional architectures to expand the application of GO. In the vacuum assisted filtrate process, both ternary GO structures and interlayer interaction between GO, PVA and ZrB_2 are achieved. The microstructures of the novel GO-PVA/ZrB_2 papers are analyzed in detail. Tensile test is employed to analyze the modulus and strength of the three dimensional GO-PVA/ZrB_2 architectures. The results show that strong materials are achieved by combining the ternary GO structures and interlayer interaction. Besides, mechanical behaviors of the novel three dimensional GO-PVA/ZrB_2 architectures are analyzed in detail.

2. Experimental

Self-assembly GO-PVA/ZrB_2 hierarchical structures: GO sheets were prepared by modified Hummer's method using graphite flakes (325 mesh, >99%, USA). Graphite flakes (3 g) and $NaNO_3$ (1.5 g) were stirred with H_2SO_4 (69 ml, 98 wt%) under an ice bath, K_2MO_4 (9 g) was slowly added into the slurry to control the temperature lower than 20 °C. Then, the first oxidation process was kept at bath temperature of 35 °C for 6 h. Before the second oxidation process, K_2MO_4 (3 g) was added again, and the reaction time was 12 h at the same temperature as the first process. After ice water (300 ml) was added, H_2O_2 (20 ml) was used to terminate the reaction. The resultant suspension was centrifuged with HCl (1 l, 5 wt%) solution and deionized water (3 l) to clean out remnant salt. GO solution (10 mg/ml) was prepared under ultrasonic for 2 h.

Pure GO papers were obtained by simple vacuum assisted filtration process. GO/ZrB_2 hierarchical structures were self-assembled by vacuum filtration method. ZrB_2 (2 μm, >99%, Northwest Institute for Nonferrous Metal Research, China) particles was high speed stirred in GO solution (10 mg/ml) for 2 h. The mixed solution was filtrated under vacuum to achieve GO/ZrB_2 hierarchical structures. The self-assembly process of GO-PVA/ZrB_2 paper was almost the same as that of GO/ZrB_2 paper. The difference was one homogeneous GO-PVA solution should be attained firstly. PVA was stirred in GO solution (10 mg/ml) for 30 min, then ZrB_2 was added and stirred for 2 h. Finally, the slurry was filtrated under vacuum to achieve GO-PVA/ZrB_2 papers.

Characterization and measurements: The microstructures of the novel hierarchical structures were characterized by scanning electron microscopy (SEM, Nanolab 600i). The graphene oxide structure was analyzed by Micro-Raman spectroscopy (Renishaw Invia, laser wavelength: 523 nm). Spectral analysis of GO and PVA was characterized by FTIR spectroscopy. Phase composition of the hybrid composites was determined by X-ray diffraction (Rigaku, Dmax-rb, CuKα 1.5425 Å). The thermal stability of the materials was characterized by thermogravimetric analyses (TGA, TA Instruments TGA 2050, USA) at a rate of 10 °C/min under nitrogen. The mechanical properties of hybrid samples were recorded with Nanomechanical testing system (UTM, Agilent T150, USA), the size of test strips was in the length among 1–2 cm and width of 0.5–1 mm. The thickness of strips varied between 20 and 40 μm.

3. Results and discussion

With the aim of analyzing the synergistic effects of ZrB_2 and PVA, both GO/ZrB_2 and GO-PVA/ZrB_2 papers were prepared through simple vacuum filtrate method. For GO/ZrB_2 papers, ZrB_2 particles were slowly added into GO solution. After the solution was stirred for 2 h at room temperature, the color of the mixture solution turned from brown to black. Through vacuum assisted self-assembly process, GO/ZrB_2 paper with ternary GO microscale structures was obtained. The difference in fabrication process between GO-PVA/ZrB_2 and GO/ZrB_2 papers was a homogenous GO/PVA solution should be formed before the adding of ZrB_2 particles. In the high speed stirring process, some ZrB_2 particles would be coated by PVA and hydrogen bond would form between GO sheets and PVA. The self-assembly process of the novel hierarchical architectures was illustrated in Fig. 1. In Step 1, the removal of solvent through the filter brought GO sheets into close contact with one another as the local concentration of the nanosheets at the filter-solvent or particles-solvent interface exceeded their solubility in water. As excess solvent was removed, the order of magnitude difference in size between the nanosheets and microparticles would prompt the formation of ternary GO structures. In step 2, since the aggregated structure was loose and weak in the axial direction, the compressive force generated by the lowering of the air-water interface and the structure undergoes compression concurrently served to reduce the spacing between nanosheets and particles, producing a highly ordered hierarchical architecture shown in Fig. 1. Moreover, multiple interactions between the three materials were formed during the self-assembly process.

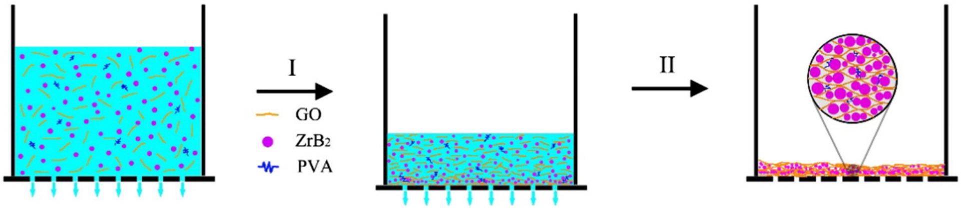

Fig. 1. Illustration of the self-assembly process of GO-PVA/ZrB_2 hierarchical architectures: step I, the formation of loose ternary structure; step II, the formation of a highly ordered GO-PVA/ZrB_2 hierarchical architecture.