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Mechanically robust and electrically conductive graphene-paper/glass-fibers/epoxy composites for stimuli-responsive sensors and Joule heating deicers

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ABSTRACT

In this article, by composing three functional constituents into a multilayered structure with well-bonded interfaces, a conductive graphene-papers (GPs)/glass-fibers (GFs) reinforced epoxy composite (GPs-GE) with outstanding mechanical robustness, high electrical conductivity and sensitive stimuli-responsive performance is highlighted. Thereinto, GPs serves as a stimuli-responsive and Joule heating chip due to its superiorities on both of mechanical and electrical properties, while GFs possessing mechanically protective and strengthening functionality. The stimuli-responsive characterizations by electrical resistance change reveal the synchronous sensing properties of GPs-GE to different stimuli inputs such as mechanical deformation, temperature fluctuation and humidity. Subsequently, Joule heating and de-icing/anti-icing properties of GPs-GE are investigated symmetrically, indicating its large heating rate, high efficiency of energy conversion and low cost. Such superior performance of GPs-GE confirms that the design of multilayer microstructure to achieve multi-functionalization paves a novel way to scale-up fabrication of advanced graphene composites, indicating promising applications as mechanically reinforcing elements, stimuli-responsive sensors and electrical Joule heating chips in intelligent engineering monitoring and icing-induced disaster prevention at low-temperature environment.

1. Introduction

With today's increasing demands to enable many multifunctional applications, such as smart sensing [1,2] and Joule heating effect [3–6] for intelligent monitoring as well as electro-thermal performance (e.g., anti-icing, fast clean-up of crude-oil and engineering mass heating) [7–9], there is an intriguing interest to seek smart and Joule heating nanomaterials with superiorities on mechanical, stimuli-responsive and electrical properties. Effective decreasing of the electrical resistance has been verified as one of the most critical routes to maximize power performance for electrical Joule heating and intelligent sensing capacity [2,5,7,8,10,11]. The state-of-the-art carbon nanostructures have been tremendously propagated in this field due to their unique physical properties, including high electrical conductivity, excellent mechanical robustness, and well manipulability for scalable fabrication, to name a few [12,13]. In general, nanocarbon assembled derivations offer novel kinds of smart and heating materials on the macroscopic scale through scale-up constructions. Particularly, paper-like graphene films (e.g., 2D scale-up monoliths of graphene sheets) are endowed with decent properties, such as mechanical flexibility, large electrical conductivity, sensitive stimuli-responsive performance and high Joule heating efficiency, suggesting great potential for intelligent sensor and electro-thermal applications.

Currently, few studies on graphene monoliths or their related composites have been reported focusing on Joule heating performance, most of which attain large heating rate and maximum

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temperature with high power inputs. For instance, Shaffer et al. reported Joule heating studies of emulsion-templated graphene aerogel with a heating rate up to 0.08 °C/s under a heating power of 1 W/cm^3 [14]. Zhang et al. fabricated graphene aerogel-based conductive polymer composite with a 3D bulky configuration and demonstrated heating rate as high as 0.796 °C/sec for power input of 12 W/cm^3 by graphene content over 1 wt% [2]. Hu et al. designed micro-sized 3D printable graphene heaters (~200 μm) with fast rates up to ~20 000 °C/sec under a power input of 5 W, and adopted carbon nanofiber-based micro-heaters to weld their micro-junctions with temperature up to 2000 °C at a heating rate of 200 °C/min [15,16]. Yu et al. employed graphene-wrapped sponge for crude-oil clean-up due to Joule heating promoted adjustment of viscosity and fast absorption under applied power reaching up to 0.58 W/cm^3 and corresponding temperature of 148 °C within 250 s [7]. However, the Joule heating and good electrical conductivity derived deicing/anti-icing and stimuli-responsive applications have not been demonstrated extensively, which are essential for these graphene materials serving in engineering applications that require intelligent monitoring and disaster preventions.

These reported Joule heating 3D graphene bulky materials have their inherent shortages in practical applications on some structural surfaces under extremely harsh serving conditions because of their poor resistance to shear stress, low strength, high brittleness, non-protective encapsulation and the difficulty of being malleable for surface covering. Therefore, 2D buckypaper-like graphene film can easily satisfy the proposed requirements for surface engineering with the coupling compliance, structural compatibility, mechanical robustness and flexibility after mechanical encapsulated protection and reinforcement by multilayered structures. Currently, 2D graphene films can be directly fabricated by chemical vapour deposition process [17], oxide paper reduction [18,19], directly aqueous dispersion [20], electrophoretic deposition [8], and roll-to-roll producing strategy [21], to name a few. The structures of graphene films are designed by controlling stacking processes and assembling orientations with a multilayered micromorphology; therefore, these materials can recover from relatively large deformations with outstanding flexibility and mechanical robustness [22]. However, the intrinsic brittleness for anti-shear force among graphene sheet in nanoscale and thin thickness induced low strength make them difficult to defeat large tensile strain, which severely restrains their widespread applications as conductive Joule heating and intelligent sensing candidates unless the structural encapsulation and mechanical reinforcement are sufficiently implemented. Therefore, in order to not only enable multi-functionalizing combinations of high Joule heating performance, intelligent stimuli-responsive behavior, excellent mechanical properties and facile electrical/structural encapsulation, but also to ensure each unit functions independently without neighboring interference, new designs of graphene composites with a multi-layered microstructure is warranted.

In this article, a conductive graphene-papers (GPs)/glass-fibers (GFs) reinforced epoxy composite (GPs-GE) was fabricated by GPs content as low as 1 wt%. Due to the intrinsically excellent electrical properties of free-standing GPs, GPs-GE inherits the similarly high electrical conductivity (3.56×10^{-3} Ω/cm) from GPs and favorably shows a significant reinforcement on mechanical properties (e.g., Young's modulus, flexure strength and fatigue resistance). The stimuli-responsive behaviors of this GPs-GE were evaluated under various stimuli-inputs, including static and dynamic periodic excitations, temperature fluctuation and humidity variation. And its outstanding Joule heating performance was verified by electro-thermal characterizations under the influence of various factors such as heating power, thermal convection and surrounding temperature. Additionally, uniform distributions of temperature fields were observed by isotropic heating mappings using infrared thermography. The Joule heating derived deicing/anti-icing performances of GPs-GE reveal large heating rate, high efficiency of energy conversion and competitive economic cost.

2. Experiment

2.1. Materials

Graphene nanoplates with average lateral diameters ranging from 0.5 to 2 μm were commercially purchased from Nanjing Xianfeng Nanomaterials Tech. Co., LTD (China) to prepare graphene ink precursor. Both epoxy resin (Tyfo® S-T Epoxy A, 1.16 g/cm^3) and amine type curing agent (Tyfo® S-T Epoxy B, 0.93 g/cm^3) were supplied by Fyfe Co. LLC (USA) with the mixture production of 1.1 g/cm^3. Polyethylene glycol octylphenol ether (Triton X-100, Average Mw ~ 80,000) was supplied by Sigma-Aldrich-China to use as a nonionic surfactant in production of GPs, and highly conductive silver paint (~5×10^3 S/cm) was purchased from Beijing Emerging Tech. Co., LTD (China) to prepare electrodes. Commercially available glass fiber tapes (GFT) were purchase from Fyfe Co. LLC (USA) with an average area density of 920 g/m^2. N-hexane and deionized water were all obtained from local suppliers (Lanzhou, China) and used as received.

2.2. Preparations of GPs and GPs-GE

2.2.1. GPs fabrication

Graphene nanoplates, obtained by a physical method [23], are employed as basic building units to prepare free-standing GPs via a vacuum filtration assisted in situ assembling process [24]. And the strong π-π interaction among graphene nanoplates provides GPs with superior electrical properties, structural robustness and fatigue resistance. In detail, as schematically illustrated in Fig. 1a, 1 g graphene nanoplates were added in 5 g Triton X-100 and mechanically stirred for 30 min. The obtained ink-like mixture was diluted in 1 L deionized water (DI water) and then dispersed to be homogenous by ultrasonic treatment (JY96 IIN, Scientz, Ningbo, China) for 30 min with a power of 100 W. Subsequently, the as-prepared graphene/Triton X-100 ink was filtrated through a microporous membrane (pore diameter = 150 nm) to facilitate graphene nanoplates self-assembling in situ into a free-standing thin film by a thickness of 20 μm under vacuum conditions. To remove residual impurities (e.g., DI water and Triton X-100 solvent) and further strengthen stacking interfaces among graphene nanoplates, the as-prepared wet GPs were transferred away from the filter membrane to anneal at 120 °C for 6 h. Finally, the obtained GPs exhibits the expected properties of high electrical conductivity, mechanical flexibility and structural robustness. Commercially purchased silver paste was then painted to fabricate electrodes with a size of $100 \times 5 \times 0.5$ mm^3 and then make electrical contact by attaching copper wires to electrodes.

2.2.2. GPs-GE fabrication

As demonstrated in Fig. 1b, the GPs-GE composite was composed of GPs, GFT and epoxy matrix. The as-fabricated GPs as an embedded conductive chip was firstly sandwiched with GFT to form a multilayered structure. To aid the infiltration process, epoxy mixture was prepared by mixing epoxy base agent, curing agent and n-hexane solvent in the ratio of 10:0.266:1 by weight and then magnetically stirred for 30 min to be uniform and clear. The multilayered GPs/GFT composite slab was then immersed into the epoxy mixture under vacuum and ice-bath conditions for 6 h to facilitate the infiltration of epoxy with trapped bubbles releasing simultaneously. Because of the good fluidic characteristics of epoxy