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Ultralight, super-elastic and volume-preserving cellulose fiber/graphene aerogel for high-performance electromagnetic interference shielding

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ABSTRACT

Ultralight cellulose fiber/thermally reduced graphene oxide (CF/RGO) hybrid aerogel with super-elasticity and excellent electromagnetic interference (EMI) shielding capability was fabricated through lyophilization and carbonization process. CF/RGO aerogel with 5 mm thickness exhibits high EMI shielding effectiveness (SE) of ~47.8 dB after annealing at 1000 °C with 5% hydrogen-argon mixture atmosphere. The superior SE is mainly ascribed to the cellular structure and good electrical conductivity of aerogel. The density of CF/RGO aerogel is as low as 2.83 mg/cm^3, leading to ultrahigh specific shielding effectiveness (up to 33780 dB cm^2/g). The volume/shape of obtained monolithic carbon material can be preserved very well after thermal treatment. The effects of RGO content and annealing conditions on EMI shielding and mechanical properties were investigated. Moreover, the hybrid aerogel possesses excellent mechanical resilience even with large strain (80% reversible compressibility) and outstanding cycling stability. In addition, adjustable EMI shielding capability could be realized by simple mechanical compression. These results demonstrate a promising and facile approach to fabricate low-cost and volume-preserving porous carbon material with superior and tunable EMI shielding performance for potential applications in aerospace and wearable electronic devices.

1. Introduction

With the development of electronic packages towards smaller and more functional, electromagnetic interference (EMI) has become an increasingly intractable task. Undesirable electromagnetic energy generated by electronic components (such as high speed processors) not only adversely degrades the performance and lifetime of these highly sensitive electronic components, but also interferes with the function of other surrounding components [1], which could lead to loss in data storage, and waste of energy and time. It is imperative to isolate these precision devices and prevent them from EMI pollution. Moreover, regular long-time exposure of living things to the environment with electromagnetic energy increases the risk of various diseases [2]. The use of mobile phones is not permitted during flight or inside intensive care units of hospitals due to EMI problem [3]. Therefore, developing high-performance EMI shielding materials is becoming an urgent challenge. Considerable amount of investigations have been conducted to improve the EMI shielding effectiveness (SE). For example, solid particles, such as ferrites, metallic magnets, conductor, and their hybrids have been introduced into polymer matrixes to fabricate EMI shielding materials due to their high permittivity/permeability and electrical conductivity [4–12]. Although satisfactory EMI shielding performance could be achieved in some cases, the disadvantages such as high loading content, heavy weight, processing difficulty and environmental degradation are still prime concerns, which severely hinder their development [13]. In addition to high-efficiency EMI SE, being light weight and flexible are another two key factors for EMI shielding materials [14], especially in areas of aerospace, modern aircraft, communication,

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flexible electronics and wearable devices [15,16].

Due to the lightweight and excellent properties of electrical and thermal conductivity, carbon aerogel, a class of three-dimensional (3D) architecture composed of sponge-like interconnected network of porous carbon has been grabbed considerable attention in recent years for electromagnetic wave suppression, especially graphene sponge [14,17,18] and carbon nanotube aerogel [19,20]. Current methods for fabricating carbon aerogel/sponge include CVD (chemical vapor deposition) [21,22] and self-assembly of nano-carbon building blocks [23,24], which inevitably involve some shortcomings, for example, high cost or toxic precursors. Besides, the complicated fabrication process and technological requirements further limit their scalability [25].

Recently, a facile approach to prepare 3D carbon sponge based on carbonization of polymer-based foam such as melamine [26–28], polyurethane [29], phenolic [30], polymide [31] and cellulose fiber aerogel [32,33] has been developed. These foams are versatile after carbonization, which have been widely investigated and applied in the fields of stretchable conductors [34], oxygen reduction reaction catalysts [33,35], supercapacitors [36], lithium-ion battery, oil cleanup [37] and EMI shielding [31,38] due to their intrinsic advantages of low cost, light weight, good elasticity, high electrical conductivity and eco-friendliness. Nevertheless, there are still some challenges to be addressed in order to remedy the drawbacks that are critical for some practical applications, for example, volume shrinkage, tunable EMI shielding performance and compressive properties. It has been reported that the volume shrinkage of cellulose fiber aerogel is up to 85% after thermal treatment [32], and the carbonization of almost all the polymer-based foams has the similar phenomenon [27,28,38], which is undesirable during the fabrication. Moreover, to reach the satisfied electrical conductivity and EMI performance, ultra-high carbonized temperature (over 2000 °C) needs to be conducted [31], which is not energy-saving. In addition, such high temperature increases the volume shrinkage [38] and decreases the compressibility. Therefore, volume-preserving aerogels with ultra-lightweight, excellent EMI shielding performance and super-elasticity are desired and of great importance.

In this work, a series of cellulose fiber/thermally reduced graphene oxide (CF/RGO) aerogels with different mass ratio were fabricated by a facile method, which involved carbonization of CF/graphene oxide (CF/GO) aerogel under different annealing conditions. Cellulose fiber possesses a large number of hydrophilic functional groups [39], which interact with GO by hydrophilic hydrophobic effect (H-bond) and promote the exfoliation and dispersion of GO in aqueous solution. More importantly, one dimensioned CF combining with two dimensioned GO sheet serve as skeleton to support the whole hybrid aerogel, which not only construct the electrical conductivity but also improve the mechanical property after annealing process. The volume and shape of CF/RGO aerogel were preserved very well after thermal treatment even annealed at 1000 °C. The ultralight hybrid aerogel possesses excellent EMI shielding capability and super high compressibility. Moreover, the EMI shielding capability of hybrid aerogel can be simply adjusted by mechanical compression, showing promise for tunable EMI shielding property. This study provides a facile and cost-effective way to fabricate volume-preserving, ultra-lightweight and super elastic carbon aerogel with excellent and tunable performance of EMI shielding.

2. Experimental

2.1. Materials

Natural graphite (~500 meshes) was provided by Yifan Graphite Factory (Shanghai, China). The oxidative agents such as concentrated nitric acid, concentrated sulfuric acid, hydrochloric acid and potassium chlorate were purchased from Beijing Chemical Factory and used as received. Cellulose fiber (CF) aqueous solution (~10 mg/ml) was supplied by Tianjin Haojia Cellulose Co., Ltd., China.

2.2. Fabrication of CF/RGO hybrid aerogel

Graphene oxide (GO) was prepared using natural graphite by modified Hummer's method [40,41]. A facile fabrication process of the hybrid aerogels was introduced in this paper. To ensure the same volume and weight of each hybrid aerogel before annealing, we set the GO concentration equal to that of CF aqueous solution (10 mg/mL). First, the weighted GO aqueous solution (10 mg/ml) was mixed with CF aqueous solution by sonication for 30 min to obtain a homogenous CF/GO solution, then, the CF/GO solution was frozen at −30 °C for 12 h and lyophilized in a freeze dryer for 48 h to obtain CF/GO aerogel. By adjusting the contents of CF and GO in the aqueous suspension, a series of CF/GO aerogels with various mass ratios of CF to GO ranging from 10:1 to 2:1 were fabricated (see Fig. S1). The final aerogel obtained from the mixed solution was referred to as CF*x*G1-YZ to show that the feeding weight ratio of CF and GO was *x*:1 and samples were thermally treated at Y °C under Z atmosphere for 5 h. Argon (A) or 5% hydrogen-argon mixture (H) were selected as the annealing atmosphere. For instance, CF4G1-800A means weight ratio of CF and GO was 4:1 and treated at 800 °C under argon, CF2G1-1000H means weight ratio of CF and GO was 2:1 and annealed at 1000 °C with 5% hydrogen-argon mixture, as shown in Fig. 2a and Fig. S1. The neat CF and GO aerogel was prepared using the same procedure with the above hybrid aerogel (see Fig. S2).

2.3. Characterization

The thickness of GO sheets was identified by atomic force microscopy (AFM, BRUKER). The morphologies of CF and hybrid aerogel were observed using scanning electron microscopy (Nova Nano SEM450, FEI). Fourier transform infrared (FT-IR) spectrum was obtained by PLATINUM-ATR ALPHA (BRUKER) between 500 and 4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS, VG Scientific ESCA Lab 220I-XL) was used to identify the elemental compositions of reduced GO and CF-graphene aerogel. Raman measurements were performed at 514 nm laser excitation (SENTERRA Micro Raman Spectrometer, Bruker Instruments). The compressive properties of aerogel were tested using a dynamic mechanical analyzer (Q800, TA Instruments) with the strain ramp of 10% per min. The electrical conductivity was calculated from the volume resistance, which was measured using a two-point probe method, as shown in Fig. S6. Each end of the sample was carefully affixed to copper foil with silver paste to reduce the electrical contact between electrode and sample. EMI shielding performance was measured in the frequency ranges of 8.2–12.5 GHz and 11.9–18 GHz at room temperature using vector network analyzer (VNA, Keysight, E5071C) combining with two waveguide-to-coaxial adaptors connected face to face. The VNA was calibrated before measurement of the *S* scattering parameter. Samples were cut into 15.8 × 7.9 × 5.0 mm and 22.9 × 10.2 × 5.0 mm (length × width × thickness) to well fit the waveguide holders with different frequency ranges, as shown in Fig. S5. Incident electromagnetic wave has power of 0 dBm, which corresponds to 1 mW. The EMI performance including SE total, SE reflection and SE absorption (SE_{total}, SE_{ref} and SE_{abs}) was calculated from the scattering parameters (S_{11} and S_{21}) [42,43].