Highly pressure-sensitive graphene sponge fabricated by γ -ray irradiation reduction

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ABSTRACT Graphene sponge (GS) with microscale size, high mechanical elasticity and electrical conductivity has attracted great interest as a sensing material for piezoresistive pressure sensor. However, GS offering a lower limit of pressure detection with high gauge factor, which is closely dependent on the mechanical and electrical properties and determined by the fabrication process, is still demanded. Here, γ -ray irradiation reduced GS is reported to possess a gauge factor of 1.03 kPa^{-1} with pressure detection limit of 10 Pa and high stress retention of 76% after 800 cycles of compressing/relaxation at strain of 50%. Compared with the carbon nanotube (CNT) reinforced GS, the improved lower limit of pressure detection and gauge factor of the GS prepared by γ -ray irradiation is due to the low compression stress (0.9 kPa at strain of 50%). These excellent physical properties of the GS are ascribed to the mild, residual free, and controllable reduction process offered by γ -ray irradiation.

Keywords: graphene sponge, piezoresistive pressure sensor, γ -ray irradiation

INTRODUCTION

Pressure sensors with high sensitivity and low price have attracted tremendous attentions due to the highly demand of electronic skin and health monitor [1–3]. Currently, pressure sensors are mainly working in the way of three different mechanisms which include capacitive sensing [4–6], piezoelectric sensing [7–9], and piezoresistive sensing [10–13]. Piezoresistive sensors, which can transduce the pressure imposed on the sensor to resistance signal, have been widely used owing to their attractive advantages, including feasible preparation, simple

device structure, and easy signal collection [11,14,15]. Pressure-sensitive materials with sufficient sensitivity in a large pressure region (from hundreds to thousands of Pa) have been used in pressure sensors [3,15–17], however seldom of them can effectively collect pressure signals at low pressure of tens of Pa, which greatly limits their applications. To improve the lower limit of the detectable pressure, sensing materials with sufficient sensitivity in lower pressure have been researched through relatively complicated fabrication processes [18,19]. Therefore, it is still a challenge to fabricate sensing materials from a simple process for piezoresistive pressure sensors that is able to detect pressure signals as low as 10 Pa.

Carbon materials have been widely used as sensing materials for piezoresistive pressure sensors, which include carbon nanotubes (CNTs) and/or graphene incorporated elastomer complexes [14,20,21], carbonized nanofibers [22], and graphene films [23,24]. In addition, conductive porous sponges or foams which are composed of graphene sheets or CNTs, can also be considered excellent alternative materials for pressure sensors [25–27]. For practical application of flexible electronics, the sensing materials in device should have a high degree of mechanical durability under loading. Sponge assembled by graphene flakes possesses high electrical conductivity, excellent mechanical and thermal properties, which holds great promise as a sensing material for piezoresistive pressure sensors with high sensitivity and excellent stability. The graphene sponge (GS) can be fabricated by chemical vapor deposition on metal template [28–30], and chemical reduction and hydrothermal reduction of graphene oxide (GO) [31–36]. However, GS fabricated

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through these methods usually presented a high lower limit of pressure detection and low gauge factor, which are determined by the elastic modulus and electrical conductivity of the sponge. For low pressure sensing with high gauge factor, a GS with low elastic modulus and large variation of electrical conductivity under compressing force is required. Chemical and hydrothermal reduction usually leaves residues at the graphene flakes, and the rigorous reduction process requiring high reduction level can cause restacking of the graphene flakes, which yields GS of high elastic modulus and low electrical conductivity. Therefore, a reduction method that can generate GS through a mild process without chemical residuals should be able to yield a sponge based sensing material with improved lower-detection limit and gauge factor for piezoresistive pressure sensor.

γ -Ray irradiation reduction is an effective and clean way to reduce GO. γ -Ray irradiates water molecules to form reductive hydrated electrons, hydrogen radicals, and oxidative hydroxyl radicals [37,38]. The oxidative hydroxyl radical can be converted to a reductive alcohol radical by oxidation radical extractant (e.g., ethanol). These reductive radicals can reduce GO to form graphene without any chemical residual. The reduction rate and reduction level of GO are determined by the γ -ray dose rate and irradiation time, which can be controlled feasibly. Plus, γ -ray has a high penetrating power, thereby allowing for a uniform reduction of GO. These merits can generate GS in a mild, uniform, and controllable process, which will be beneficial for piezoresistive pressure sensors for low pressure detection.

Here, we report a GS fabricated by γ -ray irradiation which provides a mild, residual free and controllable reduction process, and therefore, yields GS with low compression stress (0.9 kPa at stain of 50%) and excellent electrical conductivity (0.24 S m^{-1}). These physical properties are key factors, as compared with the CNT reinforced GS, for piezoresistive pressure sensing which demonstrates a gauge factor of 1.03 kPa^{-1} and pressure detection limit of 10 Pa as well as high stress retention of 76% after 800 cycles of compressing/relaxation at strain of 50%.

EXPERIMENTAL SECTION

Preparation of graphene sponge

10 mL of GO (The Sixth Element Inc.) aqueous dispersion with concentration of 2 mg mL^{-1} was diluted with 10 mL ethanol. The GO suspension was deoxygenated with nitrogen bubbling for 5 min before γ -ray irradiation

which was carried out with ^{60}Co as the light source with a dose rate of 3.12 kGy h^{-1} and irradiation time of 22 h. After the γ -ray irradiation process, the solvent of the suspension was replaced with DI water before freeze-drying. The dried GS was annealed under argon flow at 400°C for 1 h. The graphene/CNT sponge was prepared with a suspension of graphene and CNT mixture in DI water/ethanol ($v:v = 1:1$).

Structure characterization

The morphology of the samples was characterized by scanning electron microscopy (SEM, JSM-2100F) and transmission electron microscopy (TEM, JEM-ARM200F, 200 kV). Thermal gravimetric analysis (TGA) was performed on Q5000IR (TA Instruments). Raman spectra were recorded by Renishaw inVia with a 532 nm laser and $50\times$ objective lens. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a Thermo ESCALAB 250 instrument using a magnesium anode (monochromatic $\text{K}\alpha$ X-rays at 1,486.6 eV) as the source. The porosity of the samples were calculated by $\text{vol.\%} = (1 - \rho/\rho_0) \times 100$, where vol.% represents the volume porosity, ρ is the bulk density of porous GS, and ρ_0 is the density of graphite which is 2.2 g cm^{-3} .

Mechanical properties measurements

The compression performance and resistivity of the samples were tested through the UTM 2000 electronic universal testing machine. Copper leads were contacted to the sample with conductive silver paste.

RESULTS AND DISCUSSION

The scheme in Fig. 1 illustrates the chemical process of graphene reduction under γ -ray irradiation. γ -Ray decomposes water molecules to form both oxidative and reductive species. The oxidative species, hydroxyl radicals, can be eliminated by reacting with ethanol [37]. Thus, the reductive species, hydrogen radicals and hydrated electrons, react with the oxygen-contained functional groups on graphene sheets to yield reduced GO (rGO) without any byproduct. The concentrations of the reductive species in water are the function of the dose rate of γ -ray, therefore, the reduction reaction of GO is able to proceed at a steady environment that is controlled by the γ -ray dose rate. At a low dose rate of 3.12 kGy h^{-1} , the GO flakes lose their oxygen-contained functional groups and restores the conjugated carbon structure slowly to become hydrophobic. The hydrophobic force drives rGO flakes to assembly into GS that contains three-dimensional porous structure [38].

Figure 1 Schematic of the fabrication process of GS under the γ -ray irradiation.

The typical SEM images acquired at different magnifications of GS in Fig. 2a and b present interconnected pores with diameter of 100–400 micrometers inside of the GS. The pore walls are composed of assembled graphene sheets which is formed during the reduction and self-assembly process under γ -ray irradiation. The TGA curve of GO shows obvious mass decreases. The mass decrease at heating temperatures of $< 210^{\circ}\text{C}$ is primarily due to the decomposition of hydroxide groups from the GO basal plane, and the mass decrease at heating temperatures of $> 300^{\circ}\text{C}$ is mainly due to the generation of carbon oxides gases. A significant mass loss of 55 wt.% is observed for GO at heating temperature of 800°C in nitrogen. In contrast, after γ -ray irradiation, the GS presents a low mass loss of only 6 wt.% after heating to 800°C in nitrogen, indicating a high reduction level and thermal stability of GS. The Raman spectrum of GS exhibits a low signal intensity between the D and G bands and an obvious 2D band at $2,670\text{ cm}^{-1}$. In contrast to GS, the Raman spectrum of GO shows shoulder peaks at both side of the D band without 2D band (Fig. S1). The comparison between the Raman features of GS and GO indicates the restoration of the conjugated basal plane of graphene by γ -ray irradiation [39]. The chemical content of GS was studied by XPS. The C 1s spectrum of GS shows a narrow and intensive peak at 284.8 eV and one

weak peak at 286.2 eV, which can be assigned to C=C and C–O bonds, respectively. In contrast, the C 1s spectrum of GO shows a wide peak at 284.8 eV, an intensive peak at 286.8 eV (C–O), and a weak peak at 288.4 eV (C=O). The atom ratio of C/O of GS, calculated from XPS (Fig. 2e) is 9.7 which is much higher than that of GO (2.3). Therefore, both TGA and XPS analysis indicate a high reduction level of GS by γ -ray irradiation, which yield a good electrical conductivity of 0.24 S m^{-1} and a low mass density of 3.5 mg cm^{-3} (porosity of 99.84 vol.%, Table 1). γ -Ray irradiation initiates the reduction and self-assembly of graphene sheets to form GS without thermal annealing. And the post thermal annealing enhances the face-to-face staking of graphene sheets within the GS struts [40], thereby improving the compressibility and structure stability of GS for pressure sensing.

The presence of micrometer-scale pores formed by the interconnected graphene sheets yields GS good compressive properties. The stress-strain (σ - ϵ) curves of GS at maximum strains of 30%, 50%, and 80% are shown in Fig. 3a. The stress of GS increases monotonically with strain, and the σ - ϵ relationship presents three stages in the compression process. Region 1: A linear elastic region when $\epsilon < 7.3\%$ indicates the elastic bending of cell walls. Region 2: A plateau region when $7.3\% < \epsilon < 70.1\%$ where the slope increases gradually because of the elastic

Figure 2 (a) and (b) SEM images of GS. (c) TGA curves of GO and GS. High resolution XPS spectra (d) and XPS survey spectra (e) of GO and GS.

Table 1 Structure properties of graphene sponges prepared by γ -ray irradiation method

Sample	Density (ρ) (mg cm^{-3})	Porosity (vol.%)	Conductivity (S m^{-1})
GS	3.5	99.84	0.24
GS-5 wt.-%-CNT	3.6	99.84	0.26
GS-10 wt.-%-CNT	3.8	99.82	0.29
GS-30 wt.-%-CNT	4.5	99.79	0.33

buckling of cell walls. And, region 3: a steep slope region when $\varepsilon > 70.1\%$ where stress rises steeply with compression because of the densification where pore walls begin to impinge upon each other. Hysteresis loop is observed for the compressing-releasing cycle which is a typical behavior for elastomeric open-pore foams. Notably, the GS shows a low stress of 0.5, 0.9, and 4.2 kPa at strains of 30%, 50%, and 80%, respectively, which is much lower than the values in previous reports [25,41–45]. We expect that the GS with lower stress can yield a higher gauge factor (GF) for low pressure detection. In order to verify this hypothesis, we prepared CNT reinforced GS by γ -ray reduction of a mixture of GO and oxidized CNT to obtain sponges with higher stress while maintaining other structure features. The mass density, porosity, and electrical conductivity of the CNT reinforced sponges, named as GS-5 wt.-%-CNT, GS-10 wt.-%-CNT, and GS-30 wt.-%-CNT, with mass fractions of CNT of 5, 10, and 30 wt.%, respectively, are shown in Table 1, which are close to those of GS. The σ - ε curves of CNT reinforced foams are

shown in Fig. 3b and Fig. S2, which also present three regions in the compression process and hysteresis loops when releasing. Especially, the strain ranges of region 1 and 2 of both GS and CNT reinforced GSs are very close (Fig. 3c) except for the increased stress values when CNT is applied (Fig. 3d). We note that GS-10 wt.-%-CNT presents the highest stress values at strains of both 30% and 50% compared to those of GS-5 wt.-%-CNT and GS-30 wt.-%-CNT (Fig. 3), therefore, GS-10 wt.-%-CNT is applied for further studies to compare with GS. We repeated the compression-relaxation cycle on the GS and GS-10 wt.-%-CNT at strain of 50%, and the relative stress at strain of 50% is plotted with respect to the cycle number to evaluate the compression reversibility and stability of the sponges. Both GS (Fig. 3e) and GS-10 wt.-%-CNT (Fig. 3f) present a stress decay at the first 200 cycle, and maintained 76% and 83% of the initial stress, respectively, after 800 cycles of compression/relaxation, indicating excellent structure stability and compression reversibility, which are important features for pressure sensing. We note that the stress retention of GS-10 wt.-%-CNT (83%) is higher than that of GS (76%) which is owing to the hybrid structure of CNT reinforced graphene sheet where CNTs are closely adhering at the graphene sheet surface (Fig. S3) to yield improved structure stability.

To demonstrate the capability of the γ -ray reduced GS as a piezoresistive pressure sensor, the variation of electrical resistance (defined as $\Delta R/R_0 = (R_0 - R)/R_0$, where R_0 and R denote the electrical resistances of unloading and

Figure 3 The stress-strain curves (a) GS and (b) GS-10 wt.%-CNT acquired with the upper strain limits of 30%, 50%, and 80%. (c) Stress values measured at strains of 30%, 50%, and 80% of GS, GS-5 wt.%-CNT, GS-10 wt.%-CNT, and GS-30 wt.%-CNT. (d) The length of linear part in the stress-strain curves of GS, GS-5 wt.%-CNT, GS-10 wt.%-CNT, and GS-30 wt.%-CNT. Retention of the maximum stress during the 800 cycles of compression/relaxation of (e) GS and (f) GS-10 wt.%-CNT.

loading, respectively) to the applied pressure was investigated. The resistance variations of both GS and GS-10 wt.%-CNT increase monotonously with the loading at low pressure range, after which the increasing trend of $\Delta R/R_0$ increased more slowly with applied pressure (Fig. 4a). The decrease in resistance of the GS and GS-10 wt.%-CNT with the applied stress can be ascribed to the increased conduction paths as a result of the compacted sponge cells. The gauge factors (defined as $F = \delta(\Delta R/R_0)/\delta P$, where P is the applied pressure) of GS are 1.03 and 0.14 kPa^{-1} in the pressure ranges of 0–0.61 and 0.61–1.60 kPa, respectively (Fig. 4a). However, the GS-10 wt.%-CNT shows three linear response regions as shown in Fig. 4a, where the gauge factor values are 0.44, 0.82, and 0.25 kPa^{-1} , in the pressure ranges of 0–0.39, 0.39–0.81, and 0.81–1.60 kPa, respectively. The existence of two gauge factors in different pressure ranges has been ob-

served in most piezoresistive sensors, [3,10,14–19,23,24,44,45] which was ascribed to the pore volume change of the sensing materials [3]; however, systematic study is required to gain comprehensive understanding of the gauge factor dependence on the pressure range as well as the evolution of GS structure. On the other hand, the $\Delta R/R_0$ of GS increases linearly with strain of 0–50% and shows a small hysteresis when releasing the applied strain (Fig. 4b). These results indicate that GS presents a higher gauge factor in a wider linear response range and a smaller compression/relaxation hysteresis than the CNT reinforced GS-10 wt.%-CNT, especially, in the low pressure range. The improved gauge factor of GS can be ascribed to the low stress and electrical resistivity of GS at applied strain. The combination of the low stress and electrical resistivity is obtained by the γ -ray irradiation which can reduce GO at a steady environment without

Figure 4 Characterization of the resistive pressure response of graphene foam: (a) electric variation ratio change with applied pressure. (b) Resistivity change for one cycle under the strain of 50% of GS and GS-10 wt.%-CNT. (c) Detection limit test of GS. The stability test of GS under repeated loading and unloading pressure of 0.6 kPa (d) and 1.2 kPa (e).

the generation of byproduct. The resistive response of the GS under a series of pressure loadings is shown in Fig. 4c, which indicates that the GS can detect pressure as low as 10 Pa, lower than that of the GS-10 wt.%-CNT (25 Pa, Fig. S4). This detection limit is comparable or lower than the values achieved with other piezoresistive pressure sensors as shown in Supplementary information Table S1. For example, the pressure sensors with graphene film and graphene/polyurethane as sensing materials achieved detection limit of 15 and 9 Pa, respectively [18,24]. However, most of the studies achieved a sensor detection limit of >20 Pa [44,46,47–50].

The cycle tests at pressures of 0.6 and 1.2 kPa (Fig. 4d and e), which are in the two linear response regions of the resistance in Fig. 4a, were performed. The resistance shows linear response to the applied pressure and maintained consistent variation during the cycling test, implying excellent reversibility and stability.

CONCLUSIONS

γ -Ray irradiation of GO suspension generates GS under a mild and byproduct free process which yields GS with low compression stress and excellent electrical conductivity. The GS demonstrates a gauge factor of 1.03 kPa^{-1} with pressure detection limit of 10 Pa and high stress retention of 76% after 800 cycles for piezoresistive pressure sensing. By comparing with the CNT reinforced GS, we indicate that the low compression stress and good electrical conductivity of GS are important factors for piezoresistive pressure sensing.

Received 17 March 2018; accepted 15 April 2018;
published online 17 May 2018

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Acknowledgements Kong X thanks the National Natural Science Foundation of China (21503064) and Anhui Provincial Natural Science Foundation for support (1508085QE103). Xu H thanks the Ministry of Science and Technology of China (2015CB351903). Ji H thanks the 100 Talents Program of the Chinese Academy of Sciences, USTC Startup, the Fundamental Research Funds for the Central Universities (WK2060140003), and iChEM.

Author contributions Kong X, Xu H and Ji H conceived the project. Zhang T and Guo Y prepared the sponge samples. Zhang T and Wang T performed the pressure and conductivity measurements. Zhang T and Kong X drafted the manuscript. All authors contributed to the general discussion and revised the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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γ -射线辐照法制备具有良好应力检测灵敏度的石墨烯海绵材料

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摘要 石墨烯海绵具有优异的机械弹性和电导率, 其电导率在石墨烯片相互交联形成的多孔结构被压缩和释放的过程中会发生可逆变化, 因此可作为压阻传感器的敏感材料. 然而, 由于制备方法的限制使得目前报道的石墨烯海绵的压缩模量较大, 在检测低应力时材料的电导率变化不明显, 导致压阻传感器的灵敏度和检测限不足. 本文利用 γ 射线辐照还原法提供的温和、清洁的还原条件, 制备了压缩模量低的石墨烯海绵. 其作为压敏传感器的敏感材料, 实现了应变灵敏度系数为 1.03 kPa^{-1} , 检测限低至 10 Pa 、机械稳定性优异(在50%应变下800次循环最大应力保持76%)的压阻传感器.