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Multifunctional and highly compressive cross-linker-free sponge based on reduced graphene oxide and boron nitride nanosheets

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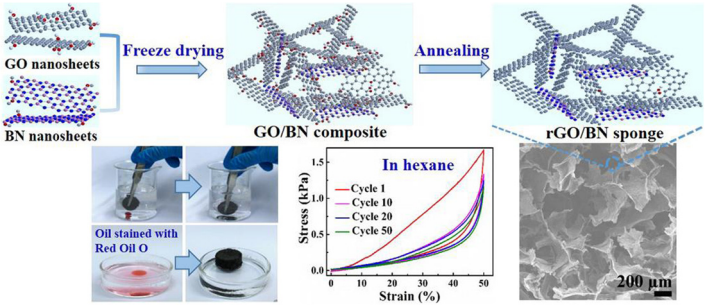
HIGHLIGHTS

- 3D cross-linker-free sponges were constructed via self-assembly of 2D GO and BN.
- The sponges featured uniform porous network and excellent compressibility.
- The sponges showed oil absorption capability of up to 170 times its own weight.
- The absorbed oil could be removed by cost effective absorption–squeezing process.
- The 3D rGO/BN sponges exhibited great promise for environmental remediation.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, we report for the first time a simple approach to fabricate 3D reduced graphene oxide/boron nitride (rGO/BN) sponges with no additional chemical cross-linkers. Encouragingly, such sponge possesses higher compressibility and better recoverability in both air and organic solvents as compared to the bare rGO sponge. The as-prepared rGO/BN sponge also exhibits excellent water resistance and high oil absorption capability, achieving up to 170 times its own weight toward a wide range of environmental contaminants. Especially, the absorbed oil can be easily removed by the absorption–squeezing process which is cost effective and environmental friendly for oil collection. Most importantly, the underlying reasons for the remarkable mechanical properties, excellent oil absorption capabilities have been analysed and revealed in depth. These exceptional characteristics together with the ease of scalable synthesis make the as-prepared 3D rGO/BN sponge show many promising applications ranging from tissue engineering, sensors, catalysis, energy storage and conversion to environmental remediation.

1. Introduction

Macroscopic three-dimensional (3D) graphene monoliths constructed by two-dimensional (2D) graphene oxide (GO) nanosheets have attracted considerable attention due to their fascinating mechanical, electrical and thermal properties [1–5].

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These outstanding properties together with the ease of scalable synthesis of 2D GO nanosheets from natural graphite make the 3D graphene monoliths show many promising applications ranging from tissue engineering [6], sensors [7,8], energy storage and conversion [3,9–12], catalysis [7,13], to sorbents for environmental remediation [14,15]. To date, a number of approaches have been devoted to the synthesis of 3D graphene monoliths such as hydrothermal-mediated reduction, template-assisted chemical vapor deposition (CVD) [1,6,19,20], chemical reduction [21,22], and freeze-drying processes [23,24]. Among them, the freeze-drying method is a relative facile and promising strategy to produce 3D graphene monoliths in a large-scale. However, additional chemical cross-linkers are usually required and most of the previously reported 3D structures undergo significant plastic deformation or have brittle mechanical performance when going through cyclic compression strain, which significantly hinders its further practical applications where 3D monoliths with unique and flexible building blocks, high porosity, as well as reversible deformation under large strain are necessary.

Currently, considerable efforts have been devoted to improve the mechanical properties of the 3D graphene monoliths, such as introducing polymers [8,25–27], carbon nanotubes (CNTs) [14,28], and metal nanoparticles [11,29] into 3D networks, while additional chemical cross-linkers are still required for most of the aforementioned cases. Notably, heterostructres self-assembled by two different kinds of low dimensional materials via van der Waals bonding in the absence of cross-linker are able to display various extraordinary optical, electronic and mechanical characteristics [30–32]. Such effective strategy has opened up new avenues for preparation of graphene-based 3D macrostructures, which are highly desirable for diverse practical applications. It is interesting that BN nanosheets (BNNSs), a new kind of 2D nanomaterials, with graphene analogous structure, show excellent mechanical, thermal and chemical stabilities, which inspire us to introduce them into graphene frameworks to reinforce the 2D structural unites, and further improve the mechanical integrity of the 3D foam structure. However, 3D interconnected heterostructre constructed from these two novel 2D materials is still at its early stage. Particularly, the reported BNNSs by the exfoliation of bulk BN in organic solvents show significant restacking or aggregation [30–32], which will significantly affect their physicochemical properties of the resultant GO/BN composite when these BN products with a non-uniform thicknesses are integrated with GO. Therefore, it is highly desirable to develop an effective approach to prepare BNNSs aqueous solution and then directly integrate the as-prepared BN dispersion with GO aqueous solution to build 3D GO/BN interconnect macrostructure with promising mechanical behaviour in a large-scale.

Based on the above considerations, in this work, we demonstrate for the first time a very simple approach for the fabrication of multifunctional 3D reduced GO (rGO)/BN sponge in a large-scale by directly freeze-drying aqueous solutions of GO and BNNSs in the absence of any additional chemical reagents. The macroscopic-assembled sponge exhibits ultralow density, high compressibility and excellent compressive recoverability in both air and organic solvents, which can be attributed to the unique 3D interconnected porous network as well as the synergistic effect between rGO and BNNSs. Furthermore, the as-prepared sponges possess high oil absorption ability (up to 170 times its own weight) toward a wide range of environmental contaminants, which are considerably higher than those of polymer [33–37] and carbon-based absorbents [38–40]. Importantly, the as-prepared 3D rGO/BN sponges show excellent flexibility and exceptional recyclability, and could be repeatedly squeezed without observable structure failure (more than 50 times), implying they are ideal candidates for environmental protection and pollution control.

2. Experimental

2.1. Preparation of GO and BNNSs

GO was synthesized from natural graphite flake (Alfa Aesar, 325 mesh) by a modified Hummers method [41]. As-prepared GO was then dispersed in water by ultrasonication for 60 min, followed by a low-speed centrifugation (3000 rpm/min) to get rid of any aggregated particles. Finally, a stable GO suspension with a concentration of 14.6 mg mL^{-1} was obtained. BNNSs was prepared by the same method as GO, except that bulk BN powder (3 *g*) was employed instead of graphite powder. BNNSs aqueous solution with a concentration of 0.6 mg mL^{-1} was obtained.

2.2. Fabrication of rGO/BN sponge

Typically, to a 10 mL beaker containing GO aqueous dispersion (14.6 mg mL^{-1}, 3 mL), BNNSs aqueous solution (0.6 mg mL^{-1}, 3 mL) was added. The mixture was homogenized in a bath sonicator for 1 h, and then placed in a refrigerator to freeze overnight. Next, the resultant GO/BN monolith was subjected to freeze-drying in a freeze dryer (Labconco FreeZone 4.5 L Benchtop Freeze-Dry System) overnight to form GO/BN sponge. Finally, the reduced GO/BN (rGO/BN) sponge with a density of 3.6 mg cm^{-3} was obtained by annealing the GO/BN sponge in a tubular furnace at 300 °C for 2 h at a heating rate of 10 °C min^{-1} in H_2 atmosphere.

2.3. Characterization

Morphology and microstructure were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F). Raman spectra were collected with a WITEC CRM200 Raman System (532 nm laser, 2.54 eV, WITec, Germany). Fourier transform infrared spectroscopy (FT-IR, IRPrestige-21 spectrometer) was acquired within wavenumber ranging from 4000 to 400 cm^{-1}. The thermal behaviours of GO, BNNSs and rGO/BN sponge were analysed by thermogravimetric analysis (TGA, Shimadzu DTG-60H thermal analyser) under a constant flow of air (50 mL min^{-1}) and heated from 30 to 1000 °C at a heating rate of 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS, Model PHI Quantera SXM) measurements were conducted for determining chemical composition of samples. Binding energy calibration was based on C 1s at 284.5 eV. The contact angle (CA) was measured on an OCA 20 contact angle system (Data Physics Instruments GmbH, Germany) at room temperature. The CA values were the average of at least four measurements at different positions on each sample, followed by calculation with ellipse fitting mode.

2.4. Mechanical test

The compressive properties of the rGO/BN sponges were measured using an Instron 5567 Mechanical Tester system at room temperature. Typically, a rGO/BN sponge with a density of 3.6 mg cm^{-3} (21.7 mm in diameter and 12.8 mm in height) was firstly loaded on the centre of the lower platen, and a compression rod with diameter of 50 mm was then applied onto the sample with a controlled speed, all the compressions were conducted within the confinement of the small upper platen. Compressive strain and stress were calculated from the displacement of the compression rod divided by original height of the rGO/BN sponge and the applied compressive force over cross-sectional area of the sample, respectively. Recoverability of the rGO/BN sponge is defined as the displacement recovered over applied displacement. The cyclic uniaxial compression data were acquired at a loading-unloading rate of 0.04 mm/min at strains of 10%, 20%, 30%, 40%