



# Compressive, ultralight and fire-resistant lignin-modified graphene aerogels as recyclable absorbents for oil and organic solvents



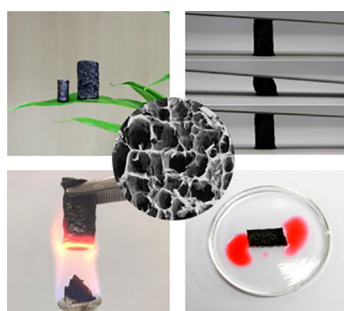
Changzhou Chen, Fengfeng Li, Yanru Zhang, Bingxin Wang, Yongming Fan, Xiluan Wang\*, Runcang Sun

Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, PR China

## HIGHLIGHTS

- Three-dimensional (3D) porous lignin-modified graphene aerogel (LGA) was fabricated by one-step hydrothermal treatment.
- The LGA was compressive, ultralight and fire-resistant with hydrophobic skeletons.
- The LGA exhibits efficient selectivity, high capacity and good recyclability for oils and organic solvents.
- The absorption capacity can be improved by carbonation treatment maximum up to 522 times.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Compressive, ultralight and fire-resistant graphene aerogel is facilely modified by renewable lignin biomass with hydrophobic and porous skeletons. The lignin-modified graphene aerogel (LGA) show highly efficient absorption of not only petroleum oils, but also toxic solvents such as toluene, chloroform and carbon tetrachloride (up to 350 times of its own weight), which is superior to that of graphene aerogel (GA) and among the highest in previous reported absorbents. Even after several compressive and release cycles, their absorption capacity are also maintained at 96%. Moreover, the absorption capacity can be further improved by carbonation treatment maximum up to 522 times of its own weight. Importantly, the LGA can be regenerated by repeated heat treatment and squeezing method, yielding almost full release of adsorbates. Such a high efficient, recyclable and renewable LGA exhibits it a potential candidate for applications in oil-water separation and also paves way to high-valued utilization of biomass waste.

## 1. Introduction

Water pollution arising from oil spills, petroleum products and toxic chemical leakage in global scale has become a major concern [1,2]. Accordingly, attentions in eliminating pollutants using high efficient absorbents are increasing. Various porous materials, including activated carbon [3], zeolites [4], wood fibers [5], polyurethane foam [6,7] and olefin resin [8,9] are considered as desirable choices. However,

most of these conventional absorbents have drawbacks, such as low absorption capacity, environmental incompatibility and poor recyclability. Very recently, low-density and highly porous three-dimensional (3D) network assembled by graphene oxide (GO) sheets have attracted considerable interests in oil-water separation. These high surface area materials normally with > 99% porosities are usually referred as reduced graphene oxide (rGO) aerogels, sponges or xerogels [10–13]. Unfortunately, pure graphene aerogels (GAs) are found to be extremely

\* Corresponding author.

E-mail address: [wangxiluan@bjfu.edu.cn](mailto:wangxiluan@bjfu.edu.cn) (X. Wang).

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brittle and non-compressive attributed to weak Van der Waal's interactions between graphene sheets. Also, converting from hydrophilic GO to hydrophobic rGO results in poor absorption capability and selectivity for polar solvents. In order to overcome these drawbacks, pure GAs are commonly modified with organic species [14,15], synthetic polymers [16,17] and carbon nanotubes [18]. Although the mechanical performance and absorption capacity of these functionalized GAs can be improved, the high cost and organic toxicity of chemical modifying agents restrict their extensive applications. Therefore, it has become urgently needed to develop cost-effective, eco-friendly and high performance absorbent materials.

As an alternative to chemical modifying agents, cheap and renewable biomass resources have emerged as an ideal absorbent materials, such as lignocellulose fiber [19,20], sugarcane bagasse [21], rice husks [22] and cellulose [23]. Among all of the biomass resources, lignin has been known as the largest natural aromatics on the earth, which is usually viewed as a waste byproduct or low value product in pulping industry [24–26]. In fact, the huge potential of lignin molecule lies in its structure, since lignin is a 3D aromatic biopolymer consists of hydrophobic phenyl propane skeleton and oxygen-contained branches [27,28]. Lignin is thus considered as hydrophobic constituent in lignocellulose, which can reduce the permeability of water across the walls of plant cells [29]. Inspired by this unique property, several attempts have been made to exploit lignin as hydrophobic feedstock in absorbent materials, such as melamine/lignin sponges [30], lignin-based xerogels [31] and lignin/polyurethane foams [32,33] with absorption capacity in the range of 19–217 times on its own weight. Incorporating hydrophobic lignin additive into 3D porous framework is one of the most promising approaches to efficiently absorb oils and organic solvents. While it is still far away from being enough to open up lignin market, much more efforts should be made to further enhance their absorption performance.

Here, we report compressive, ultralight and fire-resistant lignin modified graphene aerogels (LGAs) as efficient and recyclable absorbents for oil and organic solvents via a facile method. GO sheets with numerous oxygen contained groups (hydroxyl, epoxy and carboxyl) as precursors could link with lignin molecules through multiple intermolecular interactions such as hydrogen bondings,  $\pi$ - $\pi$  conjugation and Van der Waal's forces [34–35]. After hydrothermal treatment, interconnected networks with multi-levelled porosities are formed during the process of reducing GO. Benefiting from hydrophobic nature of aromatic lignin skeletons and porous network of graphene aerogels, the as-prepared LGA displays excellent hydrophobicity, large absorption capacity and prominent recyclability. The hydrophobic LGA has a porosity of 99.9%, exhibiting relatively high oil and organic solvent absorption capacity, 224–522 times of its own weight. Even after severely compressive-recovery cycles, its adsorption capacity can be still maintained at 96%. Such capacities are generally 3–6-fold higher than that of GA, and among the highest of previous reported lignin-based or graphene-based absorbents. This work not only provides a facile way to develop renewable and sustainable absorbent materials, but also displays promising prospects in high-valued applications of biomass waste.

## 2. Experimental section

### 2.1. Materials

Lignin from corncob was provided by Shandong Longlive Biotechnology Company. Graphite powder (> 99.8%, 325 meshes) was purchased from Qingdao Huatai Lubricant Sealing Co., Ltd. Organic absorbate including *N*-hexane, chloroform, methanol, ethanol, decane, toluene, carbon tetrachloride and petroleum Ether were purchased from Sinopharm Chemical Reagent Beijing company and used without further purification. Crude oil (1580 mPa·s, 22 °C) was provided by China University of Petroleum (Beijing, China).

### 2.2. Synthesis of GO

Graphene oxide (GO) was synthesized from pristine graphite powder according to a modified Hummers' method [36–37]. Briefly, 3.0 g graphite (Aldrich) and 1.5 g NaNO<sub>3</sub> were added into 75 mL 98% H<sub>2</sub>SO<sub>4</sub> under stirring in the ice bath. The solution was kept at 0 °C for 15 min, followed by gradual addition of 9.0 g KMnO<sub>4</sub>. Then, the resultant solution was heated to 30 °C and kept for 30 min, accompanied by slow addition of 150 mL of deionized (DI) water. After that, the mixture was heated to 90 °C and kept for another 15 min. Then, 500 mL water and 15 mL H<sub>2</sub>O<sub>2</sub> (30%) was added and the solution was filtrated using Buchner funnel, and the residue was washed by 10% HCl aqueous solution (250 mL) and DI water (500 mL). The resulting GO filter cake was dispersed in 500 mL DI water to obtain a GO aqueous suspension. Finally, GO suspension was obtained after dialysis for 7 day using a cellulose tube ( $M_w$ : 8000–14000 g mol<sup>-1</sup>). The GO sheets were obtained by centrifugation of the suspension at 4000 rpm for 30 min followed by freeze-drying.

### 2.3. Preparation of LGA

10 mg of GO was dissolved in 10 mL of 60% alcohol to form a homogeneous solution. Then a stable suspension was obtained by mixing a certain amount of lignin and GO alcohol solution using a vortex shaker (3000 rpm) for 1 min, followed by ultrasonication for 10 min. The mixture was sealed in a 16 mL Teflon-lined autoclave and heated in a muffle furnace at 180 °C for 12 h. After the autoclave was cooled to room temperature, the as-obtained hydrogel was washed with deionized water for several times, and then freeze-dried at -60 °C for 12 h to produce lignin-modified graphene aerogel (LGA). The pure graphene aerogel (GA) was also obtained according to the similar procedure.

### 2.4. Characterization

The morphology was studied using a field-emission scanning electron microscope (SEM) (HitachiS-5500). X-ray photoelectron spectroscopy (XPS) analyses were measured a photoelectron spectrometer (PHI 550 EACA/SAM) using Al K $\alpha$  (1486.6 eV) radiation. X-ray powder diffraction (XRD) patterns were recorded using a D8 Advance X-ray diffractometer with a Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The FT-IR analysis was conducted in a Thermo Scientific Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison) equipped with a liquid nitrogen cooled MCT detector. The wetting properties were evaluated through contact angle tests, which were performed by the OCA40 contact angle analyzer (Dataphysics) at room temperature. Raman spectra were recorded on a Senterra R200-L apparatus (Bruker Optics) under a 532 nm excitation laser beam. The size and thicknesses of the GO sheets were measured by an atomic force microscope (AFM) (Nanoscope III MultiMode) in tapping mode. The compression tests were carried out by using a model 3342 Instron Universal Testing Machine with two flat surface compression stages and 500 N load cells. The specific area and micro-, meso- porous size distribution were calculated by Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method using nitrogen absorption (Quadrastorb SI). The porosity and macro- porous size distribution were measured on the mercury intrusion porosimetry (MIP) (Demo AutoPore IV 9500).

### 2.5. Oil and organic solvent absorption experiments

The absorption capacities of the aerogels for oil and various organic solvents were measured according to previous procedures [11]. Typically, a weighed amount of aerogel was put into a 50 mL conical flask containing 10 mL different absorbate and allowed to absorb at room temperature for appropriate time. Then the immersed aerogel was carefully taken out and weighed after removing the surface oil or

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