3D Graphene-Oil Absorbent Resin Hybrid Gel as High Efficiency Oil Absorbent Material

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Abstract. A new type of high oil absorbent resin (OAR) was synthesized by emulsion polymerization with lauryl methacrylate (LMA) and butyl methacrylate (BMA) as soft monomers, and methyl methacrylate (MMA) as hard monomer. A graphene-oil absorbent resin hybrid aerogel (G-OAR aerogel) was therefore prepared through the hydrothermal reduction of graphene oxide colloidal solution and the oil absorbent resin emulsion. The self-assembly characteristics of graphene oxide in hydrothermal treatment resulted in the formation of 3D porous structure for G-OAR aerogel. The component, morphology and hydrophobicity of G-OAR aerogel were characterized by FTIR, XRD, SEM and contact angle, and its absorption capacities to different kinds of organic solvents and oils were also been investigated. The results indicate that the absorption capacities of G-OAR aerogel reach up to 40-50 g/g for low density organic solvents, like acetone, anhydrous alcohol, cyclohexane, toluene, ethyl acetate and diesel. The absorption capacities are 80-90 g/g for high density and weak polarity organic solvents, like phenixin and castor oil. The good oil absorption property makes it show high potential in the application of wastewater treatment and oil leakage.

1. Introduction
In recent years, oil spills triggered by industrial accidents have caused catastrophic damage to marine and river ecosystems [1]. How to remove or collect the oil slick quickly and thoroughly without causing secondary pollution is an urgent problem still unresolved [2]. Extensive researches have been carried out till-now to explore new methods for effective oil-water separation, and the usage of high-performance adsorbent materials have been proven to be a most effective one [3]. Among various oil adsorbent materials, graphene aerogel is considered as an ideal adsorbent material due to its high porosity, large specific surface area, low density, strong hydrophobicity and friendly-environment [4]. However, graphene aerogel is mechanically weak and brittle under stress, which seriously limits its practical application [5].

According to previous reports, embedding polymer in the 3D network of graphene aerogels will produce high-performance and multi-functional nanocomposites [6]. The high oil-absorbing resin is a new type functional polymer material [7], which has many merits, like low density, good oil-water selectivity, fast oil absorption rate, high oil absorption capacity, and high strength etc.
In order to overcome the shortcomings of graphene aerogel, we incorporate graphene with acrylic ternary oil absorbent resin. By taking the advantages of synergistic effect between graphene and oil absorbent resin, a new oil absorbent material with high oil absorbent capacity and high strength is proposed. So far, there has been no literature reporting on graphene and high oil absorbent resin composite aerogel materials.

In this paper, an acrylate-based oil absorbing resin was prepared by emulsion polymerization, and incorporated with graphene to prepare a 3D porous graphene-oil absorbing resin hybrid aerogel (G-OAR aerogel) through hydrothermal treatment (Figure 1). The composition, morphology and hydrophobicity of G-OAR aerogel were analyzed by FTIR, XRD, SEM, contact angle, etc., and its absorption capacities for different kinds of organic solvents and oils were also investigated.

Figure 1. The fabrication process and photo of G-OAR aerogel.

2. Experimental

2.1. Chemicals
Lauryl methacrylate (LMA), butyl methacrylate (BMA), methyl methacrylate (MMA), nonylphenol ethoxylate-10 (OP-10), sodium dodecyl sulfate (SDS), ammonium persulfate (APS), divinylbenzene (DVB) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of ternary oil absorbent resin
4 g LMA, 2 g BMA, 4 g MMA, 0.1 g SDS and 0.1 g OP-10 were dispersed in deionized water, stirred until dissolving, and then ultrasonicated for 20 mins to form a homogeneous pre-emulsion. 0.2 g APS was dissolved in deionized water as initiator solution.
The polymerization was carried out in a 250 mL four-necked flask equipped with mechanical stirrer, a condenser, a thermometer, and an inlet of nitrogen. 1/3 pre-emulsion, 1/3 APS initiator solution and 0.24 g crosslinker DVB were placed into the flask, and heated to 75 ºC. The remaining pre-emulsion and initiator solution were added dropwise into the system simultaneously using constant pressure dropping funnel. This dropping process lasted for 1.5-2 h, and then the temperature was raised to 80 ºC. The pH was adjusted to 4-6 using NaHCO₃ aqueous solution and the amount of the NaHCO₃ aqueous solution should guarantee the water-oil volume ratio in the reaction system to be 3:1. After reaction for 4 h, polyacrylate emulsion-based oil absorbent resin was obtained as a milky white colloid.

2.3. Preparation of grapheme-oil absorbent resin hybrid aerogel
Grapheme oxide (GO) was prepared according to Hummers’ method with slight modifications [9], and made up a colloidal solution with a concentration of 5 mg/mL.

10 mL grapheme oxide colloidal solution (5 mg/mL) and 10 mL ternary oil absorbent resin emulsion (5 mg/mL) were mixed and ultrasonicated for 0.5 h to form a homogeneous suspension. The suspension was then transferred to a Teflon lined stainless steel autoclave and reacted at 180 °C for 3 h. Then the reactor cooled naturally to room temperature, and the hydrogel cylinder was took out and washed carefully with deionized water. After freeze-drying, the three-dimensional grapheme-oil absorbent resin composite aerogel (G-OAR aerogel) was obtained.

Grapheme aerogel was prepared following the similar way via hydrothermal reaction with grapheme oxide as precursor.

3. Results and Discussion

3.1. Characterization
Figure 2A shows the FTIR spectrum of grapheme oxide, G-OAR aerogel and grapheme aerogel. Comparing with grapheme oxide, G-OAR aerogel exhibits two peaks at 2925 cm⁻¹ and 2853 cm⁻¹, which are ascribed to the stretching vibration of methyl and methylene at the backbone of ternary copolymer. In addition, the peaks at 1195/1148 and 1729 cm⁻¹ are associated with the stretching vibrations of C-O groups and the C=O (ester) groups in the acrylate precursor [10]. Figure 2B displays the X-ray diffraction pattern of G-OAR aerogel and grapheme aerogel. Compared with the grapheme aerogel, G-OAR aerogel has a new peak at the diffraction angles of 10-15°, indicating there are other low-crystalline component existed besides grapheme. The as-prepared ternary oil-absorbing resin with low-crosslinking belongs to this low crystallinity substance. According to the FTIR and XRD results, ternary oil absorbent resin is successfully composited with grapheme aerogel.

Figure 2. (A) The FT-IR spectra of grapheme oxide (a), G-OAR aerogel (b), grapheme aerogel (c). (B) The XRD of G-OAR aerogel (a) and grapheme aerogel (b).
Figure 3A-C displays the SEM images of G-OAR aerogel at different magnifications. It can be seen that G-OAR aerogel shows a 3D porous structure with pore size at micrometer scale. Oil absorbent resin particle (average diameter below 200 nm) disperse uniformly at the surface of graphene layer, no obvious aggregation are observed. The contact angle of G-OAR aerogel is 102.1° (Figure 3D), which indicates its strong hydrophobicity. In Figure 3E, a 250 g counterweight is placed on a 30 mg G-OAR aerogel, and its overall shape is not severely deformed and collapsed, hence it can withstand at least 8333 times of its own weight. Under the same conditions, the graphene aerogel is crushed, so G-OAR aerogel is mechanically strong.

![Figure 3](image)

**Figure 3.** (A-C) The SEM images of G-OAR aerogel in different magnification. (D) The water contact angle measurement of G-OAR aerogel. (E) Mechanical strength test of G-OAR aerogel (left) and graphene aerogel (right).

### 3.2. Oil absorption test

Since G-OAR aerogel exhibits unique structural and interfacial properties, including hierarchically porous structure, large specific surface area and strong hydrophobicity, it processes good absorption capacity for organic solvents. Here, diesel, phenixin, castor oil, ethyl acetate, ethanol, toluene, cyclohexane and acetone are chosen as representative solvents to investigate its absorption capacity. Briefly, for those solvents with high polarity or low density, like diesel, ethyl acetate, ethanol, toluene, cyclohexane and acetone, the absorption capacities are about 40-50 g/g (Figure 4). For phenixin and castor oil with weak polarity and high density, the absorption capacities are about 80-90 g/g.

Table 1 shows the comparison of the saturated absorption capacities of G-OAR aerogel, graphene aerogel and ternary oil-absorbing resin for diesel, toluene and phenixin. It can be seen that the absorption capacity of G-OAR aerogel for organic solvents and oils is higher than that of oil-absorbing resin and graphene aerogel, which identifying the synergistic effect of graphene and oil-absorbing resin in G-OAR aerogel.
Table 1. Comparison of oil absorption ability (g/g) of oil absorbent resin, grapheme aerogel and G-OAR aerogel.

|          | OAR | G-A | G-OAR gel |
|----------|-----|-----|-----------|
| diesel oil | 9.8 | 38.2 | 48.2      |
| toluene   | 20.2| 37.3| 47.2      |
| phenixin  | 33.5| 67.6| 85.8      |

Figure 4. The oil absorption properties of G-OAR aerogel.

4. Conclusion
In conclusion, a ternary copolymer was synthesized as high oil absorbent resin through emulsion polymerization. A grapheme-oil absorbent resin hybrid aerogel was prepared via hydrothermal reduction self-assembly of grapheme oxide colloidal solution and oil-absorbing resin emulsion. The hybrid aerogel possesses many advantages, like 3D porous structure, large specific surface area, strong hydrophobicity, and therefore showed good absorption capacity for organic solvents. The results indicate that the absorption capacities for acetone, absolute ethanol, cyclohexane, toluene, ethyl acetate and diesel are about 40-50 g/g, and absorption capacities for castor oil and phenixin with high density and weak polarity is about 80-90 g/g, which makes it one of the most efficient materials currently reported. Therefore, we envision that graphene-oil absorbent resin hybrid aerogel could work as a highly efficient adsorbent material in wastewater treatment and oil leakage.

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