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Abstract

As the depletion of traditional fossil fuels and environmental pollution become a serious problem of human society, researchers are actively finding renewable green energy sources. Considered as a clean, efficient and renewable alternative, Hydrogen energy is considered the most promising energy source. However, the safe and efficient storage of hydrogen has become the major problem that hinders its application. To solve this gap, this paper proposes to utilize surfactant modified graphene for hydrogen storage. With Hummers method and ultrasonic stripping method, this study prepared graphene from graphene oxide with NaBH4. Surfactant sodium dodecylbenzene sulfonate (SDBS) was used as a dispersant during the reduction process to produce the dispersion-stabilized graphene suspensions. The characteristics of the graphene suspensions then were examined by XRD, SEM, TEM, FT-IR, Raman, XPS, TG, and N_2 adsorption-desorption tests. The hydrogen adsorption properties of the samples were investigated with Langmuir and Freundlich fitting. The results show that the adsorption behavior is consistent with the Freundlich adsorption model and the process is a physical adsorption.

Keywords: Surfactant; Graphene; Hydrogen storage; Adsorption.

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1. Introduction and literature review

Energy and environment are two major issues that mankind urgently needs to solve. With the depletion of traditional fossil fuels and serious environmental pollution, researchers come to an agreement on the necessity of alternative clean and renewable sources. Hydrogen energy is recognized as one of the most ideal energy source for its cleanness, efficiency, and renewability [1–5]. As hydrogen is unstable, to safely and efficiently store hydrogen becomes the critical barrier for its wide application. Proper hydrogen storage should have high energy density, low energy consumption, and high safety. Scientists use mass storage density and volume storage density are two major indicators of hydrogen storage.

Many researchers have developed extensive and profound studies on the hydrogen storage technology. One of the research direction is the storage materials, which can categories the hydrogen storage as physical adsorption and chemisorption. There are four main type of adsorption materials, including carbon hydrogen storage materials, non-carbon nanotubes materials, mineral porous materials, and microporous metal–organic framework [6]. Among them, the carbon hydrogen storage material is insensitive to a small amount of gaseous impurities and can be used repeatedly. In addition, they have low atomic mass, high chemical stability, and rich tubing structures [7–12]. Carbon hydrogen storage materials also have subcategories, including super activated carbon, nanostructured carbon materials, and graphene [13]. Graphene is considered as the prospective new carbonaceous hydrogen storage material with highest potential due to its unique physical and chemical properties and simplicity of preparation.

The preparation technology of graphene has made great breakthroughs in past decades, the latest research mainly focuses on increasing the specific surface area of graphene materials. Srinivas et al. oxidized graphite with a Hummers method, followed by ultrasonic stripping in water to form graphene oxide, and then reduced hydrated hydrazine to produce graphene [14]. Under a pressure of 1000 kPa and temperatures of -196 °C and 25 °C, the absorbed amount of hydrogen can reach 1.2 wt.% and 0.1 wt.%, respectively. Ghosh et al. produced graphene with thermal exfoliation of graphite oxide at high temperature [15]. The results show that the hydrogen adsorption capacity was about 2.0-3.1 wt.% at 10,000 kPa and 65 °C. Cheng et al. reported that the hydrogen adsorption capacity of graphene reaches 0.4 wt.% and 0.2 wt.% at 100 kPa, -196 °C, 6000 kPa, and 25 °C, respectively [16]. In addition, a large amount of graphene preparation studies show that ,due to agglomeration, the actual specific surface area of the produced graphene is much smaller than its theoretical value (6.0 wt.%) that suggested by the US Department of Energy. Therefore, this study aims to obtain a stable graphene suspension and prepare high-quality single-layer graphene to improve hydrogen adsorption.

Graphene has low hydrophilicity and lipophilicity, and there exists van der Waals force between the layers, which tends to cause agglomeration. Without preprocessing, it is difficult to obtain monolayers and aqueous solutions or organic reagents. The dispersion of graphene may form lumps and agglomerates and further deteriorate its performance after drying. Therefore, it is necessary to improve the hydrophilicity or lipophilicity of graphene so that the formation of composites and other substances can be reduced. In recent years, researchers found that the surface of graphite oxide contains many active groups, such as carbonyl groups, carboxyl groups, epoxy groups, and etc. These groups can react with other substances, making the modification of graphene feasible. The modification of graphene has the same mechanism as carbon nanotubes and fullerenes that active groups on the surface of the crystal leads to active graphene surface. In general, the modification methods for graphene mainly include surface modification, chemical doping, functionalization of a polymer base, and physical modification. Bourlino et al. utilized amino siloxane and amino acid for the modification, and modified graphene can maintain stable in water [17]. Niyogi et al selected octadecylamine (ODA) as a modifier to synthesize long-chain alkylated graphene on the surface of graphite oxide [18]. The modified graphene can stably disperse in tetrahydrofuran and carbon tetrachloride solution. Chen et al. used the graphene sulfonation method, which can not only improve the graphene, but also well maintain the various excellent properties of graphene [19]. This method first uses the sodium borohydride to allow reduction-oxidation reaction and sulfonate the produce in an ice bath for 2 hours, then the bisamine was used as a reducing agent for chemical reduction. Liang et al. used charge repulsion to obtain a well-dispersed graphene suspension in water [20]. Niyogi et al. reported that octadecylamine can be used to treat long-chain alkyl modified graphene [18]. Based upon aforementioned studies, this paper aims to propose a new method to prepare high quality graphene for the purpose of hydrogen storage.

2. Methodology

2.1. Materials and apparatus

The experiment equipment and materials are summarized in following Table 1 and Table 2.

Table 1. Chemicals used in the experiment

Name	Chemical Formula	Molecular Weight	Level	Producer
Flake Graphite	C	12.01	325mesh, 99.8%	Alfa Aesar Tianjin Chemical Co.,Ltd
Potassium Permanganate	$KMnO_4$	158.04	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd
Strong Sulfuric	H_2SO_4	98.01	95.0-98.0%	China Sinopharm Chemical Reagent Co., Ltd
Hydrogen Peroxide	H_2O_2	34.01	30%	China Sinopharm Chemical Reagent Co., Ltd
Potassium Perchlorate	$KClO_4$	138.56	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd
Muriatic acid	HCl	36.56	36-38%	China Sinopharm Chemical Reagent Co., Ltd
Sodium Borohydride	$NaBH_4$	37.85	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd
Sodium Nitrate	$NaNO_3$	84.99	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd
Acetone	CH_3COCH_3	58.08	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd
SDBS	$C_{18}H_{29}NaO_3S$	348.48	Analytically Pure	China Sinopharm Chemical Reagent Co., Ltd

Table 2. List of apparatus

Equipment	Producer
Sartorius Electronic Scales	Beijing Sartorius Instrumentation System Co., Ltd
DHG-9070A Electro-thermostatic Blast Oven	China Shanghai Yiheng Science and Technology Ltd
SHZ-D Circulating Vacuum Pump	China Gongyi Yuhua Instrumentation Co., Ltd
KQ-500VDF Ultrasonic Generator	China Kunshan Ultrasound Instrumentation Co., Ltd
IKL RCT Basic Magnetic Stirrers	China Shanghai Yiheng Science and Technology Ltd
HC-3518 Centrifuge	China USTC Chuangxin Co., Ltd

2.2. Preparation of surfactant modified graphene

(1) Preparation of graphite oxide

The modified Hummers method was used to prepare graphite oxide. First assemble a 500 ml reaction flask in an ice water bath. Mix 5 g of graphite powder and 5 g of sodium nitrate with 200 ml of concentrated sulfuric acid. Add 25 g of potassium perchlorate while stirring, and then add 15 g of permanganate. Ensure the temperature will not exceed 20 °C, once done, remove the ice bath and transfer the reaction bottle to the electromagnetic stirrer, electromagnetic stirring for 24 h. After that, 200 ml of deionized water should be added slowly, and raised up the temperature to about 98°C. After stirring for 20 minutes, an appropriate amount of hydrogen peroxide was added to reduce the remaining oxidizing agent to make the solution bright yellow. The graphite oxide suspension was then centrifuged at a rate of 10,000 rpm and washed successively with 5% HCl solution and deionized water until the pH of the separation solution was set to 7. The obtained cake was vacuum dried to obtain graphite oxide.

(2) Preparation of graphite

After the graphite oxide was pulverized, disperse 300 mg graphite oxide in 60 ml of deionized water to obtain a brownish yellow suspension. A stable colloidal suspension can be obtained after ultrasonic dispersion for 1 h. Then transfer the suspension to a four-necked flask and add 600 mg of sodium borohydride and 50 mg of sodium dodecylbenzenesulfonate under 80°C. After refluxing for 16 hours, then centrifug and wash the mixture with

acetone and deionized water until pH=7. The obtained filter cake was vacuum dried and stored for future use, which was denoted as GS1. Use the same method but prepare graphene without dispersing agent and marked the sample as GS.

3. Results and discussion

3.1. Physical properties

(1) XRD characterization

Fig. 1 shows the XRD characteristics of graphite (G), graphite oxide (GO), graphene (GS1 / GS). It can be seen that the crystal plane diffraction peak of graphite is very strong and sharp at 2θ of 26.58°, indicating that the graphite sheet is not spatially aligned.
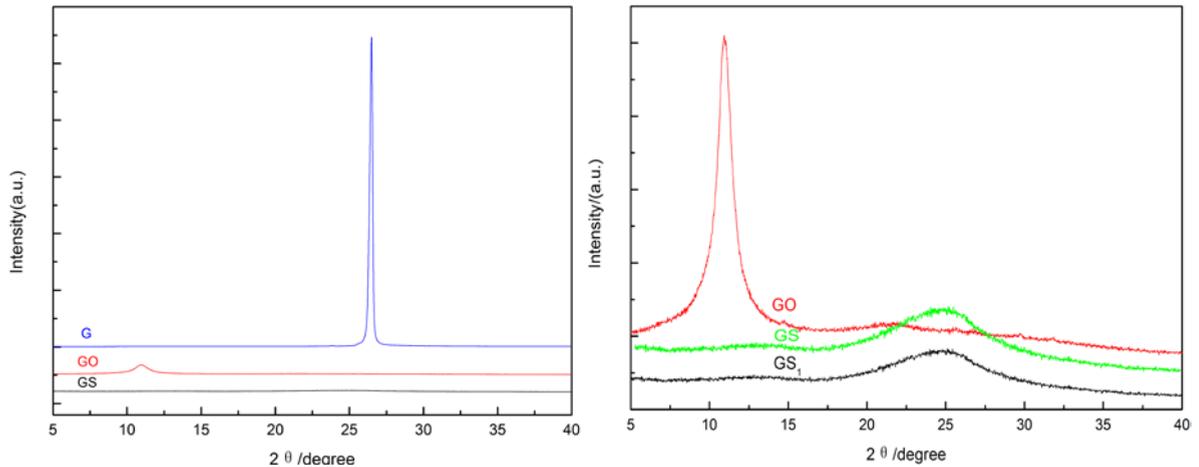

Fig. 1. XRD pattern of G, GO, and GS (left) and XRD magnification of GO, GS1, and GS (right)

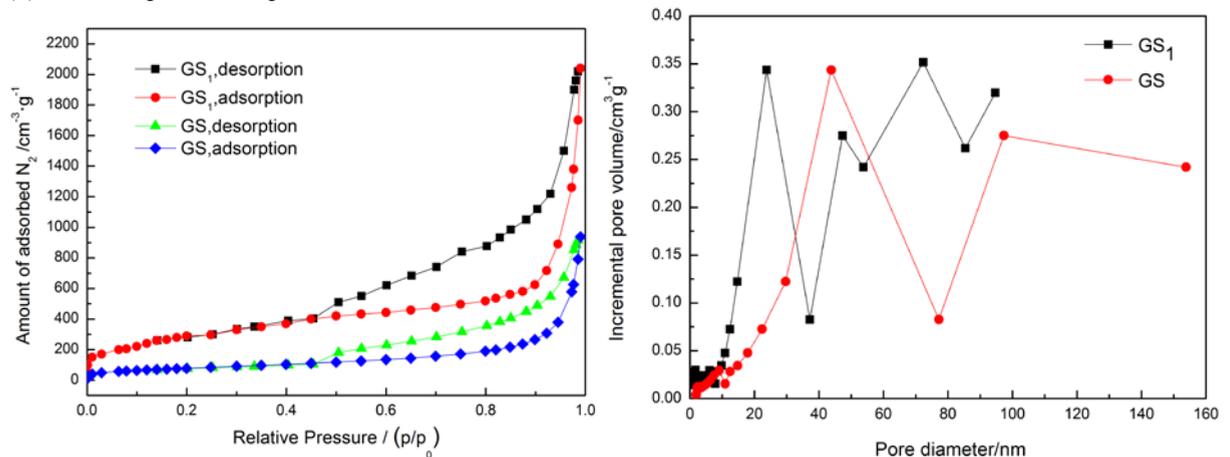(2) N_2 adsorption-desorption characterization

Fig. 2. N_2 adsorption-desorption isotherms of GS1 and GS (left) and pore size distributions of GS1 and GS (right)

Fig. 2 show the N_2 adsorption-desorption isotherms and pore size distributions of graphene samples GS1 and GS at liquid nitrogen temperature, respectively. From the figure, the isotherm shows a type I adsorption curve and a hysteresis loop appears on the isothermal adsorption-desorption curve at a relative pressure of about 0.4, which

results in a narrow gap between graphene layers. The specific surface area of graphene sample GS1 (about 1206 m2·g-1) is much larger than the specific surface area of GS (605 m2·g-1), but smaller than the theoretical surface area of single layer graphene (2630 m2·). This shows that the graphene sheet GS1 has both single-layer graphene and double-layered structure, however, compared to previous studies, the specific surface still significantly improved. The pore size distribution in Fig. 2 also shows that the pore size of GS1 is smaller than GS, and the number of micropores is also larger than GS. This explains why the specific surface area of GS1 is larger than that of GS.

3.2. Hydrogen storage capacity fitting

   (1) Langmuir Model

$$\frac{p}{V^a} = \frac{1}{V_m^a b} + \frac{p}{V_m^a} \tag{1}$$

Where Vma is the saturated adsorption amount, Va is the actual adsorption amount, and b is the Langmuir adsorption constant. Vma and b can be estimated with regression slope and intercept.

   (2) Freundlich adsorption model

$$\lg V^a = \lg K + n \lg p \tag{2}$$

Where Va is the actual amount of adsorption (ml/mg) under pressure, K is the reaction rate constant, and n is the empirical constant. The size of n indicates the ease of adsorption, smaller n means better adsorption ability, while larger n indicates more difficult adsorption. In general, when n is between 0.1 and 0.5, the adsorption is easy to perform, when n>2, adsorption is more difficult. Fig. 3 shows the results of both fitting model.
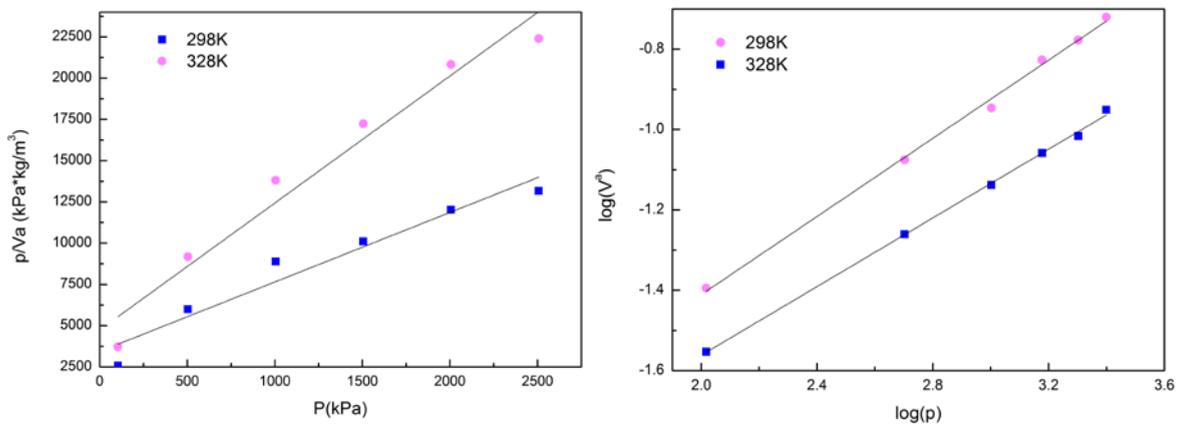

Fig. 3. Hydrogen adsorption capacity of graphene with Langmuir model (left) and Freundlich model (right)

4. Conclusions

This paper proposed a high-efficiency hydrogen storage graphite preparation method based on liquid-phase oxidation. After ultrasonic peeling, a high-quality graphene sheet was prepared by adding dispersant sodium dodecylbenzenesulfonate during the reduction process. The structure, morphology and composition of the samples were characterized by XRD and N_2 adsorption-desorption isotherms. The both Langmuir and Freundlich adsorption model fitting shows that the adsorption of hydrogen on graphene occurs first in the micropores and hollow structures of graphene at low pressure.

Acknowledgements

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