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Easy Synthesis of Light-weight Hierarchical Mesoporous Carbon Sponges for Efficient Oil Spill Recovery

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Abstract

The clean-up of spilled viscous crude oil has increasingly become a global challenge. Since the rather limited sorption speed restricted the use of traditional oil sorbents materials in practical oil-spill remediation, people gradually pay more attention to the nanoporous materials and technology to clean-up viscous crude oil by turning the rheology through Joule-heating. Herein, we report a quite easy synthesis method to prepare light-weight nanoporous carbon sponges by using the cheap environmentally friendly melamine foam, a widely used and mass disposal building material with high porosity of over 99%, as the template and carbon source. SEM images show that the natural 100 μm level porous network structure of melamine foam retained after the carbonized carbon sponge material. Nitrogen adsorption-desorption isotherms as well as the corresponding pore size distribution results clearly indicating the unique hierarchical mesoporous features of the as-developed carbon sponge, which is good for its contact with the spill oil. XRD and Raman spectra verified the partial graphitization characteristics of the mesoporous carbon sponges, FT-IR and XPS spectra confirmed the presence of N and O containing functional groups. The Joule-heating performance in a simulated oil spill case under sunlight show that the obtained mesoporous carbon sponges superior than supported graphene control (MF-G) on the heating and rheological regulation effect, thus is an excellent candidate for oil spill recovery. The synthetically balanced physicochemical characteristics and additional merits such as low cost, enriched oxygen-containing functional groups, good bulk electrical conductivities and robustness make this carbon sponge material a good platform for the development of various advanced multifunctional materials for oil spill recovery.

Keywords

Carbon Sponges; Oil Spill Recovery; Hierarchical mesoporous; Graphitic Carbon

Introduction

As one of the most important natural resource to humanity, the crude oil has obviously improved the civilization development and of the living quality of human inhabitants of the earth. However, frequent oil-spill accidents, which usually happened during the oil exploration and transportation processes, can cause serious disaster to marine ecology.[1] Besides, an increasing leakage of viscous industrial residual oil (such as burning residual fuel in marine diesel generator and industrial waste heavy oil) to the sea also threaten ecological security and human health.[2] In view of the present increasingly serious marine environment pollution by oil spills, it is of high priority for researchers to develop advanced materials and technologies for the efficient clean-up of viscous residual heavy oil. Currently, there are three types of available technologies for oil-spill remediation: i) chemical methods (in situ burning, dispersants, solidifiers), ii) bioremediation and iii) mechanical recovery (booms, skimmers, sorbents). For a long time, researchers focus on the sorbent materials which can remove the spill oil in situ from the water surface. [3] However, most of the reports on the traditional oil sorbents suffers from low oil/water separation efficiency/speed and high materials cost, thus restricted their practical applications in real oil-spill remediation. [4]

Nowadays, the demand for the repair materials developed as the understanding of oil-spill remediation engineering grows. During the past ten years, there are two giant oil-spill accident all over the world, both of which rank the top 10 oil-spill accidents all

over the human history, one is the 2010 Gulf of Mexico oil spill, the other one is the 2018 Sanchi oil spill nearby Shanghai, China. [5-7] It may be surprising for most people that even the estimated oil release amount are both huge (4.9 million barrels in 2010 Gulf accident, 1.0 million barrels in 2018 Sanchi accident), the ecological damage to the local marine ecosystem of the Sanchi accident is significantly smaller than that caused by the Gulf accident. In fact, most of the residents in Shanghai were unaware of such a major oil spill accident, even though they live only 160 nautical miles from the accident location. The main reason is that the oil released in 2018 Sanchi accident is mostly condensate oil (C5 to C11) , which can easily evaporate into the atmosphere within one hour when exposed on the sea surface and thus be natural diluted, leading to a very limited amount of residual oil on the sea surface. That means, viscous oil and unviscous oil are quite different, and perhaps we do not need to absorb every drop of spilled oil by sorbent materials as usually proposed to realize the spill oil remediation. A more reasonable and economical way is to adjust the volatility and rheology of spilled oil, then it can natural volatilization or can be easily removed by normal mechanical booms or skimmers at an extremely low cost. In terms of current human technology, the in-situ modification of volatility of oil on the sea surface seems very hard since it can only occur under high-temperature and high-pressure condition, however, the regulation of rheology of spilled oil is quite possible. The basic principle is that the crude oil can be heated and softened continuously by the Joule heating effect on the contact interface of the heating material and the adsorbed crude oil, thus aroused the good Joule heating ability of the oil-spill remediation engineering materials. In view of this, the porous carbon materials with enough mechanical strength seems the best candidate.

For the past decade, many works on the advanced sorbents for oil-spill cleanup have been developed, in which carbon materials are an important family of sorbent materials. In recent years, the carbon sorbents have been extended from traditional activated carbon to the nanostructured carbon nanofibers, CNTs and graphene architectures. For example, Wang et al. reported a facile dip-coating method to prepare rGO/melamine foam nanocomposites as a novel sorbent to achieve fast collection of crude oil from spills.[8] Gui et al. successfully developed a ferrocene based chemical vapor deposition method to prepare the hydrophobic porous magnetic carbon nanotube aerogel with a mass-sorption capacity for diesel oil of 56 g g⁻¹. [9] At the same time, carbon materials have shown great Joule heating ability, in which an over 80% high photothermal conversion efficiency can be easily achieved. [10] In addition, the mechanical strength and durability of carbon foams are also acceptable regarding the sea wave condition. [11] To the end of efficient spill-oil recovery by turning their rheological property, all the above-mentioned factors must be involved in the consideration, thus the synthesis of ideal comprehensive multifunctional spill-oil recovery materials are still a big challenge.

Until now, there are already some pioneering work employing carbon foam or carbon sponges with multiple functions as electrochemical energy storage materials [12], solar steam generation and desalination materials [13] and piezoelectric materials [14], yet have not been widely used in the field of spill-oil recovery though Joule heating. Very recently, Yu et al. developed a Joule-heated graphene-wrapped sponge (GWS) to clean-up viscous crude oil at a high sorption speed. The Joule heat of the GWS reduced in situ the viscosity of the crude oil, which prominently increased the oil-diffusion coefficient in the pores of the GWS and thus speeded up the oil-sorption rate. [15] This in situ Joule self-heated sorbent design is obviously a fundamental work in promoting the practical application of hydrophobic and oleophilic

oil sorbents in the clean-up of viscous crude-oil spills, even the high cost of graphene and the applied voltage working mode restricted the industrial applicability and practical application potential.

Based on the above discussion, to the end of efficient spill-oil recovery by turning their rheological property, our concept is to use the carbon sponges directly derived from melamine-formaldehyde foam by fast calcination at 800 °C. Compared with the melamine foam supported graphene (MF-G) control, our hierarchical mesoporous carbon sponge material has obvious advantages in heat production and viscosity turning. Although the oil adsorption capacity of this carbon sponge is slightly lower than control, its comprehensive performance well meets with all the design requirements for Joule heating oil spill recovery material. Further study mechanical tensile showed its engineering applicable mechanical strength and durability. The carbon sponge material reported in this work is an excellent platform for the subsequent development of a variety functional materials and engineering technologies for oil spill recovery.

Results and Discussion

Materials design and morphology

As discussed above, the new understanding of spill oil recovery engineering based on Joule heating lead to the more complex and balanced requirement of recovery materials. Besides the three basic requirements described above (good oil contact and flow interface, excellent Joule heating ability and ideal mechanical strength and durability), some additional desirable properties for spill-oil recovery is also welcomed, such as the adjustable hydrophilicity and lipophilicity, electrical conductivity and corrosion resistance. [16,17] For example, most carbon materials

are natural hydrophobic, this is no problem in the simple oil-water separation application but cannot accommodate to either the further functional assembly and modification with other hydrophilic components or the rapidly changing conditions in spill-oil heating and recovery sites. Even the nanostructured graphene-based materials can hardly fully satisfy each requirement, not to mention the high cost of graphene regarding scalable environmental remediation applications. Therefore, the choosing of the template and precursor for the porous carbon materials with considerable adjusting potential and low cost is crucial.

Inspired by the recent work reported carbon foam or carbon sponges derived from melamine-formaldehyde resin foam and applied in the fields of electrochemical energy storage and piezoelectric material[12,14], we believe the environmentally friendly melamine foam, a widely used and mass disposal cheap building material with a low density of 8-10 mg cm⁻³ and a high porosity of over 99%, is an excellent candidate template and carbon source for the design and construction of ideal carbon sponges towards spill oil recovery based on Joule heating effect. Considering the previous experiences in the synthesis of porous carbon materials with good mechanical strength and durability based on melamine foam, we applied the easy synthesis strategy of directly fast calcination of melamine foam at 800 °C, the experimental details can be seen in the experimental section.

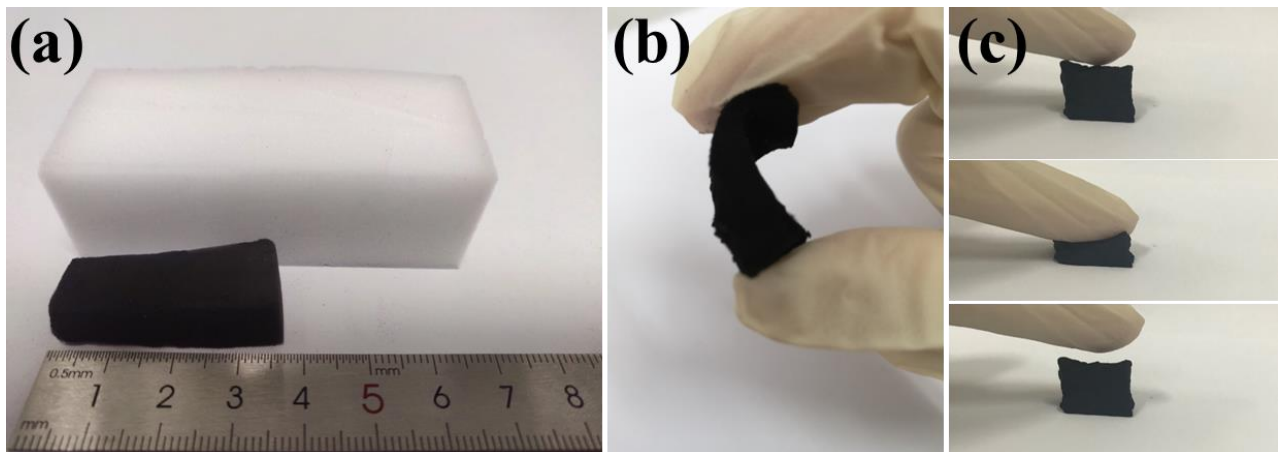


Figure 1: The (a) physical photos of raw melamine foam and as-prepared carbon sponge derived from melamine foam with good flexibility (b, c).

The physical photos of the melamine foam raw material and the as-developed MF carbon sponge materials was shown in Fig. 1a. After the fast carbonization treatment at 800 °C for 0.5 h, the block volume of the MF carbon sponge decreases to approximately 10% of the raw melamine foam, while the weight yield of the carbon sponge from the melamine foam is approximately 12-15%, indicating the partial flow away of the N-enriched thermal decomposition products followed by the Ar gas flow, which can also reflected by the asymmetrical shape of the carbon sponge block and may benefit to the maintenance of network structure and mechanical strength when the volume decreased. The light-weight feature of the material (approximately 12 mg cm⁻³) make it possible for the carbon sponge to be floating on the crude spill oil. The simple blending and restrain experiment as shown in Fig. 1b and Fig. 1c illustrated the good flexibility of the as-developed MF carbon sponge materials. The mechanical tensile test with a strain rate of 0.1 mm/s show the Young's modulus of the as-developed MF carbon sponge was 26.7 MPa, verifying the good mechanical strength and durability of the obtained MF carbon sponge, which can well satisfy the supposed wave environment of water surface. [18]

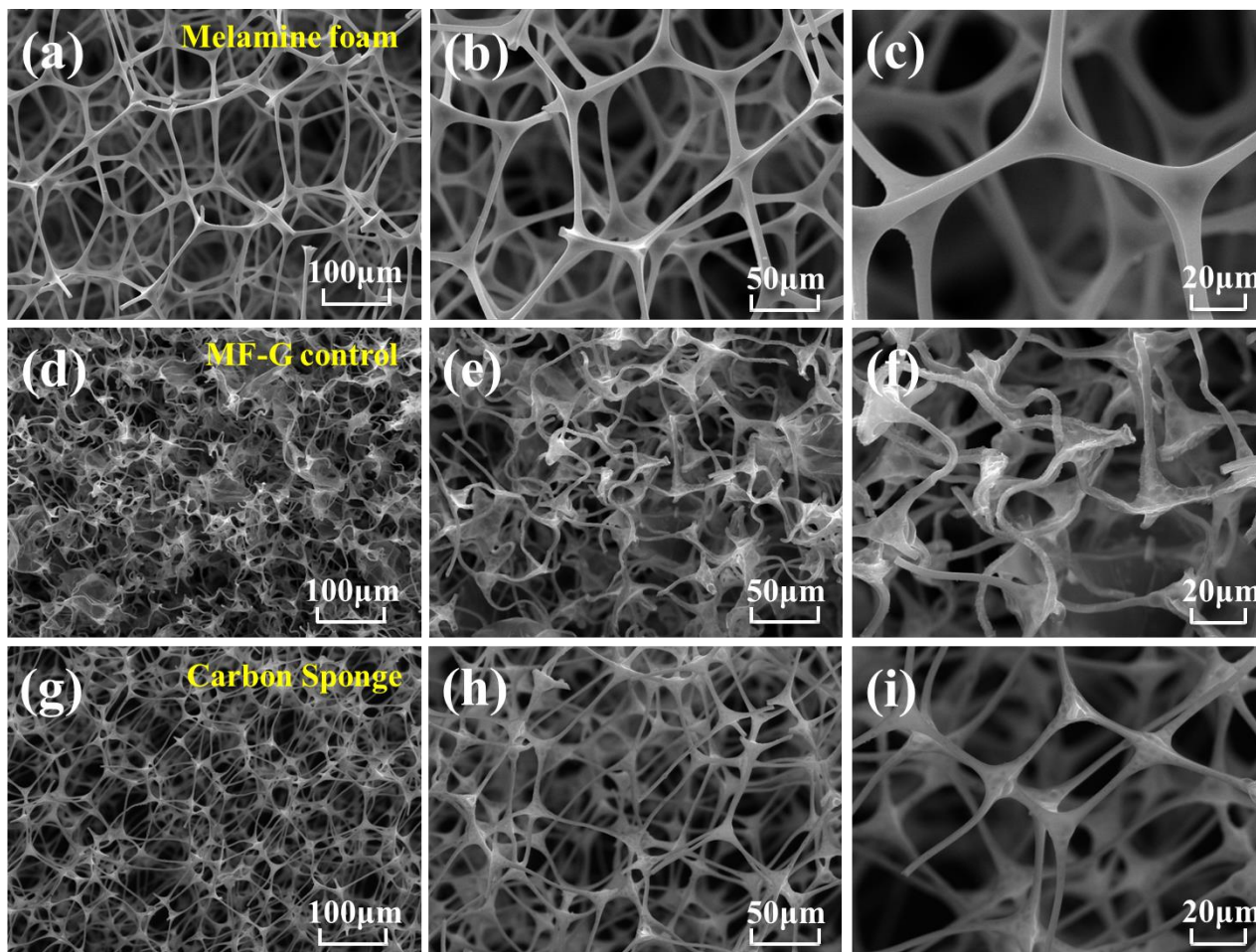


Figure 2: The SEM images of (a-c) raw melamine foam, (d-f) MF-G control and (g-i) carbon sponge.

Fig. 2 reveal the SEM images of the raw melamine foam, MF-G control and as-prepared MF carbon sponge. As shown in Fig. 2a-c, the melamine foam has innate interconnected fiber network porous structure with a typical pore size of 100-200 μm . The SEM images of the MF-G control (Fig. 2d-f) clearly show the uniformity dispersive graphene supported on the MF network, which slightly decreased after the impregnation and drying process. This kind of material are believed to be with high Joule heat property and relatively low cost because of the use of cheap MF as support. Fig. 3g-i shows the SEM image of a typical carbon sponge carbonized from MF under an Ar atmosphere. Remarkably, the innate interconnected nanofibers network architecture of the melamine foam well restrained except for the size

shrinkage due to thermal polycondensation, which is superior than most reported carbon foam materials in porosity and structural integrity.

Physicochemical characteristics

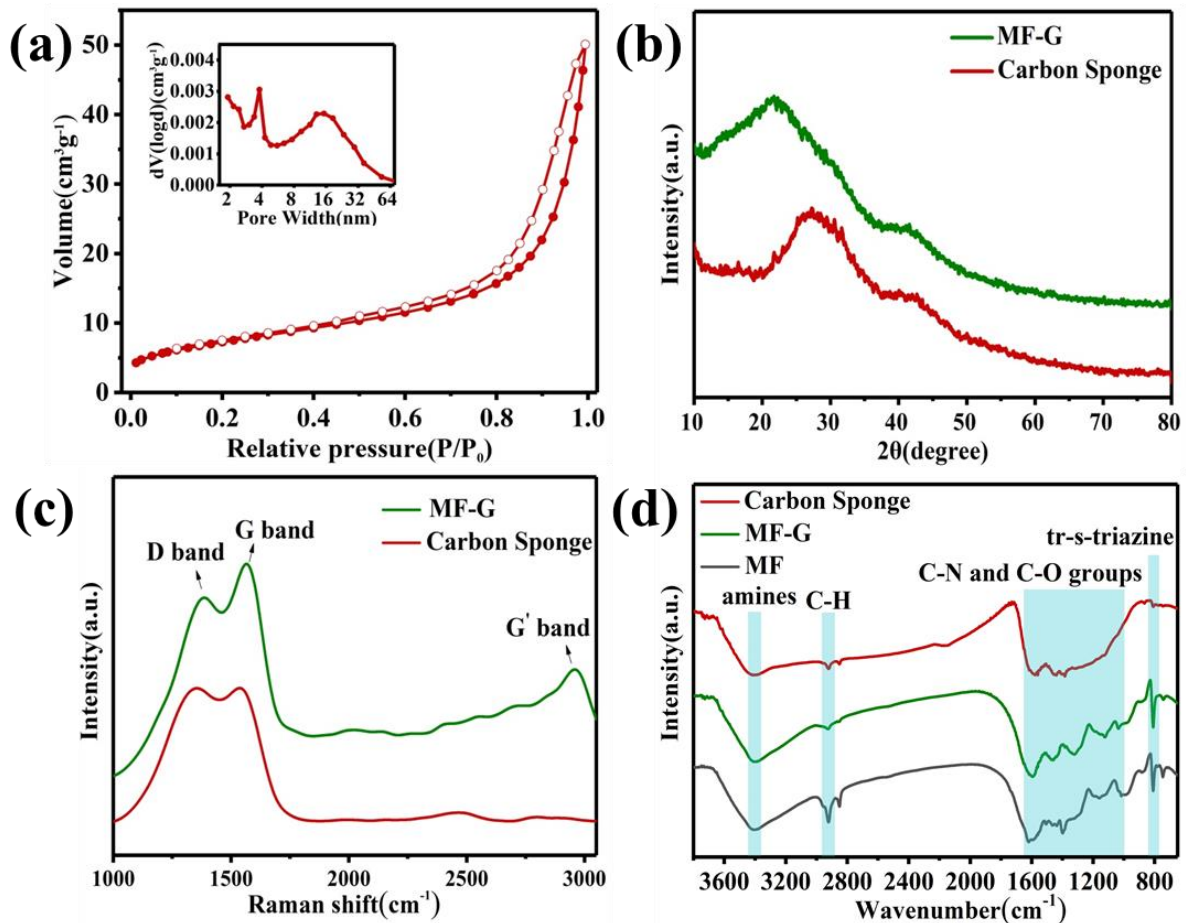


Figure 3: (a) Nitrogen adsorption-desorption isotherms and corresponding BJH pore size distribution curves of as-developed carbon sponge; (b) XRD, (c) Raman and (d) FT-IR spectra of MF-G control and MF carbon sponge.

Fig. 3a exhibits the nitrogen adsorption-desorption isotherms and corresponding BJH pore size distribution curves of as-developed carbon sponge to investigate its nanoporous features, in which a typical type IV isotherm with a clear hysteresis regression line at relative pressure range of 0.70-0.99 can be observed, which is characteristic of capillary condensation in mesoporous. The pore size distribution curves reveal the unique hierarchical mesoporous features (3.9 nm and 17 nm) of this

material, which is profitable for its contract with the spill oil. The hierarchical mesopores maybe generated during the carbonization process lies in the release of N_2 and NH_3 , since the molecular formula ($C_3H_6N_6CH_2O$) of the raw MF foam material contains a lot of nitrogen atoms and hydrogen atoms. [19] The X-ray diffraction (XRD) pattern (Fig. 3b) of MF-G control and MF carbon sponge both illustrate two broad peaks at about 26° and 43° , which can be indexed to the (002) and (100) plane of graphitic carbon (PDF#75-1621), respectively. The graphitization degree of the two sample were further identified by Raman spectra (Fig. 3c), in which typical characteristic peaks of G-band (vibration for all sp^2 bonded carbon atoms) and D-band (the vibrations of carbon atoms with dangling bonds) of graphitic carbon at around 1360 and 1590 cm^{-1} can be clearly identified, respectively. The G' band at 2950 cm^{-1} presented the origin of graphitic carbon in the MF-G control is from additional graphene, which is different from that of the MF carbon sponge by directly carbonization of melamine foam. The calculated $I_{G/D}$ value of MF carbon sponge is 1.13, further indicating its good graphitization state.[20] In consequence, the as-developed MF carbon sponge possesses a good electrical conductivity with a measured value of $2.9 \times 10^{-3}\text{ S cm}^{-1}$, thus open wide potential for the further design of spill oil recovery electrochemical devices. [21]

As shown in Fig. 3d, the surface function groups of the as-developed MF carbon sponge were characterized by FTIR compared with the raw melamine foam and MF-G control. The peaks locate at 810 , 2930 and 3400 cm^{-1} can be ascribed to the vibration of tri-s-triazine, C-H and amine groups, respectively. The wide peaks approximately range from 1000 to 1620 cm^{-1} are the C-N and C-O related characteristic peaks. It can be seen that the tri-s-triazine peak in the FTIR spectra of

melamine foam and MF-G control disappeared in the spectra of MF carbon sponge sample, indicating the melamine related tri-s-triazine structure was thermal decomposed and serve as carbon source of carbon. The presence of amino group stretching near 3400 cm^{-1} implicit its good controllable hydrophily which is hard to obtain in common carbon materials. Overall, the as-developed MF carbon sponge material contained numerous nitrogen and oxygen containing functional groups, which can officiate the fast gas adsorption and mass transfer during spill oil recovery applications.

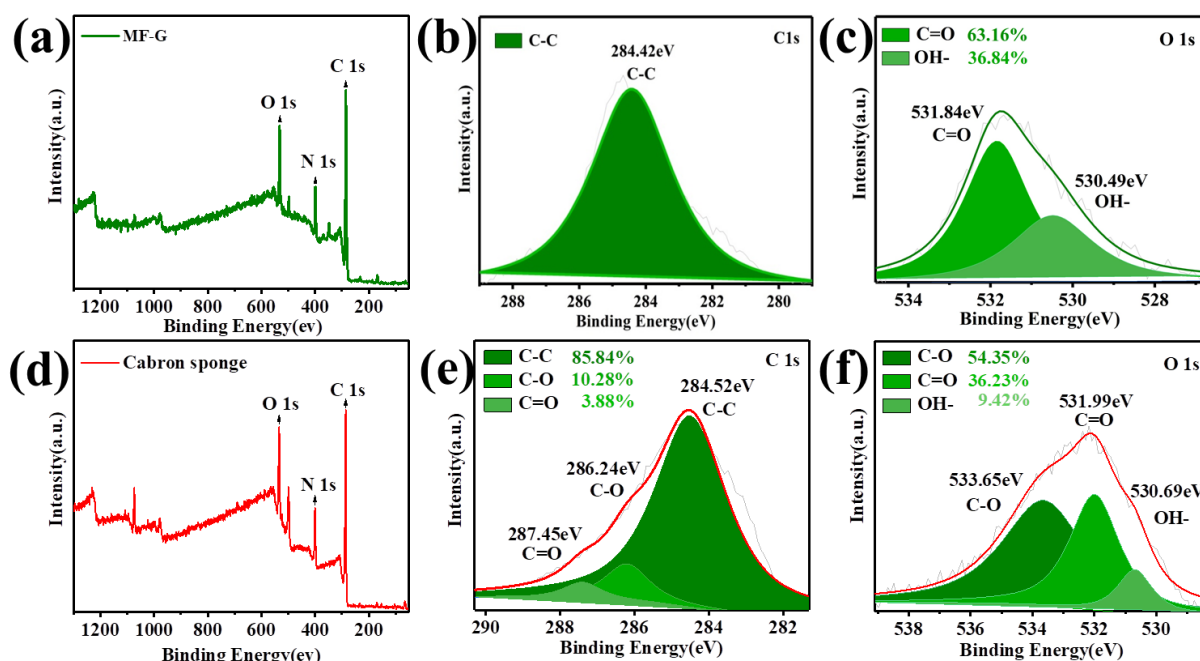


Figure 4: (a-c) survey XPS spectra and high-resolution C 1s and O 1s XPS spectra of MF-G control, (d-f) survey XPS spectra and high-resolution C 1s and O 1s XPS spectra of MF carbon sponge.

To further characterize the chemical composition of MF-G control and MF carbon sponge, X-ray photoelectron spectroscopy (XPS) analyses were performed. The survey XPS spectra of the two samples reveal that they are both composed with C, N and O, which are all enriched in the melamine foam. This presence of N-containing functional groups contributes in its good bulk electrical conductivities. The high-

resolution C 1s spectra of MF-G control show only a simple C-C peak, while its high-resolution O 1s spectra only show the presence of C=O and -OH structure organed from the basic components of the melamine formaldehyde resin. However, the high-resolution C 1s and O 1s spectra of the MF carbon sponge both show an obvious new C-O signal except the above-mentioned peaks, which may be caused by the carbonization process of melamine formaldehyde resin and in good accordance with the FT-IR results. The enriched oxygen-containing functional groups provides great potential for further modification in develop spill oil recovery devices. [22,23]

Oil spill recovery performance

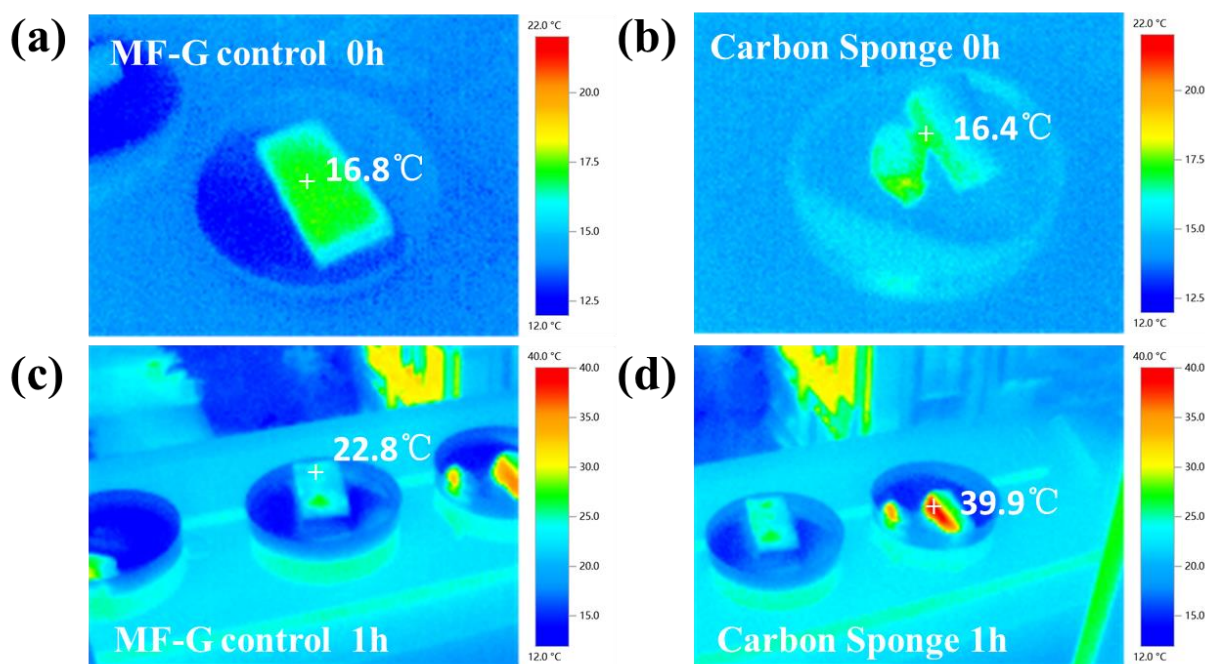


Figure 5: The Joule heating thermograph over MF-G control and as-prepared MF carbon sponge before and after practical sunlight irradiation (450 W/m²).

Table 1: Comparison of rheological properties of spill oil after treatment with MF-G control and as-prepared carbon sponge for 1h under sunlight.

Sample	ΔT (°C)	Kinematic viscosity (mm ² /s)	Oil adsorption capacity (g/g)
MF-G control	6.0 °C	54.2	134.8

Carbon sponge	23.5 °C	45.8	106.9
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Based on the above mentioned structural and physicochemical properties, the oil spill recovery performance of the carbon heating materials powered by the solar energy was tested in a simplified but practical model experiment, in which the MF-G control and the as-developed MF carbon sponge and the MF-G control with a weight of 0.13 g and a bulk size of approximately 15 cm³ was placed in the central of a plastic petri dish filled with 1/3 of water and 1/3 of liquid paraffin oil and directly exposed to air under sunshine with a irradiation intensity of 450 W/m² to simulate the water-oil-gas three-phase environment in the oil spill sites. As can be observed from the Joule heating thermograph, both MF-G control and as-prepared MF carbon sponge heating material and the surrounding oil are cold (16.4-16.8 °C) at 0 h. After practical sunlight irradiation for 1 h, the MF-G control Joule heating material only show a limited 6.0 °C temperature rise, while the as-developed MF carbon sponge show a much superior 23.5 °C temperature rise. As a result, the kinematic flow viscosity of the surrounding oil also decreased from the initial value of 58.1 mm²/s, and a better flow viscosity of 45.78 mm²/s can be achieved in the MF carbon sponge treated oil, indicating the Joule heating effect of the MF carbon sponge in situ reduced the viscosity of the oil, which prominently increased the oil-diffusion and thus may speeded up the oil-sorption or pumping process. [24,25] Although the oil adsorption capacity of this carbon sponge (106.9 g/g) is slightly lower than MF-G control (134.8 g/g) due to its non-super lipophilic properties, its oil adsorption capacity are good even among carbon sorbents, thus is large enough for comprehensive spill oil treatment. The comprehensive performance of the MF carbon sponge better compliance to the design requirements for Joule heat oil spill recovery material than conventional graphene-based materials. Benefited from its unique balanced physicochemical

characteristics and additional merits such as enriched oxygen-containing functional groups and bulk electrical conductivities, we believe that this kind of high porosity, ultralight weight and robust carbon sponge material can be a good basic material for the development of a variety functional oil spill recovery materials and engineering technologies. [26-28]

Conclusion

In summary, we fabricate a flexible nanoporous carbon sponge material by using the cheap melamine foam as raw material. The obtained MF carbon sponge is composed of a uniform 3D interconnected partially graphitized carbon nanofibers network with a good mechanical strength (Young's modulus 26.7 MPa), and displays a unique hierarchical mesoporosity. The presence of oxygen-containing functional as verified by FT-IR and XPS spectra improved the balanced and controllable hydrophilicity and lipophilicity of this kind carbon sponge materials. Consequently, the Joule-heating performance of this unique hierarchical mesoporous MF carbon sponge which merits of low cost and durable was quantitative analysed by record the thermographic temperature difference and flow viscosity of oil in a simulated oil spill case under sunlight, in which the MF carbon sponge show a superior temperature increasement and viscosity turning performance over the supported graphene control MF-G, as well as a high oil adsorption capacity of 106.9 g/g, indicating its great potential in addressing the problem in oil-spill remediation. The cheap raw materials, simple fabrication process and satisfactory performance make our materials promising for many further spill oil recovery devices and technologies.

Experimental

Materials preparation

Typically, in order to obtain the ideal carbon sponge materials, the raw melamine-formaldehyde resin foam was cut it into small pieces with size of 60*30*20 mm, then three pieces of this tailored melamine foam was placed in the centre of the quartz tube one-by-one closely. Only the central piece after carbonization is the designed product, while the other two pieces serve as the sacrificial air flow stabilization materials during the carbonization process at high temperature. More concretely, the quartz tube cavity was purged by Argon gas for 1h, then heated from room temperature from room temperature to 800 °C steadily in 1h and kept at 800 °C for 0.5h, then cooled naturally in the slow Argon flow atmosphere (50 ml/min). The final product was a light-weight, flexible and tailorable black foam, which is named as MF carbon sponge in this work. In order to compare the spill-oil recovery properties of the as-developed MF carbon sponge materials with common reported high-performance supported graphene materials, we also prepared the MF-G control materials by stirring the cutted melamine foam pieces in 100 mL graphene dispersion (0.5 mg/mL, purchased from XFnano Technology Co., Ltd., China and use as received) at room temperate for 2 h to natural adsorption saturation state, then the black monolith was dried in air in an drier oven at 80 °C overnight and used as MF-G control.

Materials characterization

A scanning electron microscope (SEM, Philips XL-30FEG) was used to observe the morphology structure. Nitrogen adsorption-desorption isotherms were measured on a Accelerated Surface Area and Porosimetry System (ASAP2460, Micromeritics) at 77 K. X-ray diffractometer (XRD) patterns were scanned in θ -2 θ mode using a Bruker D8 Advance diffractometer (Cu $K\alpha$ 1 radiation, λ = 1.5406 Å) operated at 40 kV and 40 mA (scanning step: 0.02 °/s). Raman spectra were obtained in a HORIBA LabRAM HR Evolution Raman microscope using a 532 nm argon ion laser. The Fourier transform infrared (FT-IR) spectroscopy on KBr pellets of the samples were recorded

by Thermo Scientific Nicolet iS50 FTIR Spectrometric Analyzer. X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha) with Al Ka radiation was employed to characterize the chemical bonding state. The mechanical performance was measured by an ElectroForce test instrument with a strain rate of 0.1 mm/s (3200 Series II, Bose, USA).

Evaluation of the oil spill recovery performance

The Oil spill recovery experiment over the carbon heating materials powered by the solar energy was performed in a simplified but practical model, in which the MF carbon sponge and the MF-G control (both weight 0.13 g with a materials-oil contact area of approximately 10 cm²) was placed in the central of a plastic petri dish with heat insulating mattress, which was then filled with 1/3 of water and 1/3 of liquid paraffin oil (with a density of 0.845 g/cm³, purchased from Wuxi Yatai Chemical Co., Ltd., China and use as received) to simulate the water-oil-gas three-phase environment similar with that of the oil spill accidents. The experiment was carried out at high noon without obviously cloud in March at Shanghai (N 31°21', E 121°33'), the solar irradiation intensity was 400-500 W/m², which is a mild sunshine energy that can be received in most places of the world. The temperature of the heating materials was record by tacking the thermograph of materials by using the Testo 869 infrared thermal imager. The flow viscosity of the liquid paraffin oil before and after the treatment was measured by using a standard flow cup viscometer method.

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