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# Hydrophobic and fire-resistant carbon monolith from melamine sponge: A recyclable sorbent for oil–water separation

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## ABSTRACT

Here we report a new strategy for fabrication of macro/mesoporous carbon monolith from commercially available and low-cost melamine sponge. This synthesis route involves the cooperative self-assembly and coating of block copolymer mixed with resol on the melamine sponge, followed by pyrolysis at different temperatures. The as-fabricated carbon monolith exhibits high porosity and excellent hydrophobicity, thus can be used as a potential sorbent for the removal of oil from water. The intrinsic fire-resistant property of obtained carbon monolith makes it a recyclable sorbent for oil–water separation. More importantly, benefiting from the low-cost, available raw material and simple synthesis route, the production of the carbon monolith can be easily scaled up. This work offers a simple pathway to prepare carbon monolith, which is a promising candidate in the field of oil spill cleanup.

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## 1. Introduction

With multiple interconnected macropores and mesopores, carbon-based hierarchical porous monoliths have extensively enhanced properties compared with single-sized porous carbons, and show good application future in the fields of absorption, catalysis, sensor and so on [1–3]. In particular, the high porosity and good physical and chemical stability of porous carbon monolith make it a feasible sorbent for the removal of contaminants. For example, Prussian blue-decorated carbon sponge, used as a sorbent for targeting internalized radiocesium and other radionuclides in human body, exhibits binding affinity and selectivity to radionuclide targets [4]. Magnetically-separable porous carbon, fabricated

via in situ self-assembly of latex spheres and block copolymers with resins and Ni species, shows a high absorption capacity for organic dye, such as methylene blue [5].

Wettability of a solid surface is one of the important characteristics influencing its application. In consideration of the role of wettability in oil–water separation, the design of special wetting materials has attracted great attention [6,7]. One of the most well-known “lotus-effect” is attributed to a connection of chemical composition and surface roughness on multiscale lotus leaf surface [8]. Consequently, inspired with this natural phenomenon, one way to enhance the hydrophobicity of materials is to fabricate micro/nano-scale structure including the superposition of two roughness patterns at different length scales [9,10].

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Hierarchical porous carbon monoliths with superior wettability have attracted more and more attention. These materials used in oil spill area have facilitated a phase change of oil from liquid to semisolid, leading to the removal of oil from water just by pulling out the porous sorbent [7,11]. For instance, hierarchical porous carbon synthesized via hydrothermal process followed by a nanocasting pathway has been applied to the collection of oil from water [12]. In our lab, we have developed a biomimetic 3D ordered multimodal porous carbon by integrating colloidal crystal, block copolymer and phenolic resin, and has successfully used it as a sorbent for the removal of paraffin oil from water [13]. However, the costly and complicated fabrication procedures, harsh practical conditions, low stability and flexibility dramatically hamper the mass production of carbon monoliths for practical applications. Therefore, it is an urgent need to explore a low-cost and time-saving pathway for the preparation of hierarchical porous carbon monoliths to overcome the aforementioned limitations.

To date, there is a trend to the mass fabrication of carbon-based materials from commercially available polymeric sponges due to their low cost and rich source. As the common types of household cleaning pads, polyurethane (PU) and polyvinyl-alcohol (PVA) sponges with 3D macroporous structure have exhibited a high absorption capacity for both water and oil [14,15]. However, the poor thermostability and low fire resistance of PU and PVA sponges have restricted their applications in daily life. Thus, melamine sponges with high nitrogen content have attracted much attention due to their unique fire-resistant property [16]. When exposed to fire,

released nitrogen from melamine can retard burning, reducing the risk of fire and explosion when used as sorbent for flammable oils and organic solvents.

Herein, we report a facile approach to design hydrophobic and fire-resistant macro/mesoporous carbon monolith from commercially available melamine sponge (see Fig. 1). This synthesis route involves the cooperative self-assembly and coating of block copolymer mixed with resol on the melamine sponge, followed by pyrolysis at different temperatures. The as-made carbon monolith can effectively absorb oil from water with good recyclability. More importantly, the production of the carbon monolith is easy to be scaled up due to the low-cost, available raw material and the simple fabrication method. The obtained carbon monolith exhibits excellent hydrophobicity, high porosity and intrinsic fire-resistance, making it a promising candidate to the field of oil spill cleanup.

## 2. Experimental

### 2.1. Materials and chemicals

Commercial melamine sponge was purchased from BASF. Pluronic F127 (PEO-PPO-PEO) was purchased from Sigma-Aldrich. Coal oil and diesel oil were provided by China National Petroleum Corporation. Vegetable oil and peanut oil were purchased from local supermarket. Oil paint (lake blue 455#) was purchased from Marie Painting. Other chemicals were obtained from Shanghai Chemical Corporation. All reagents were used without further purification.

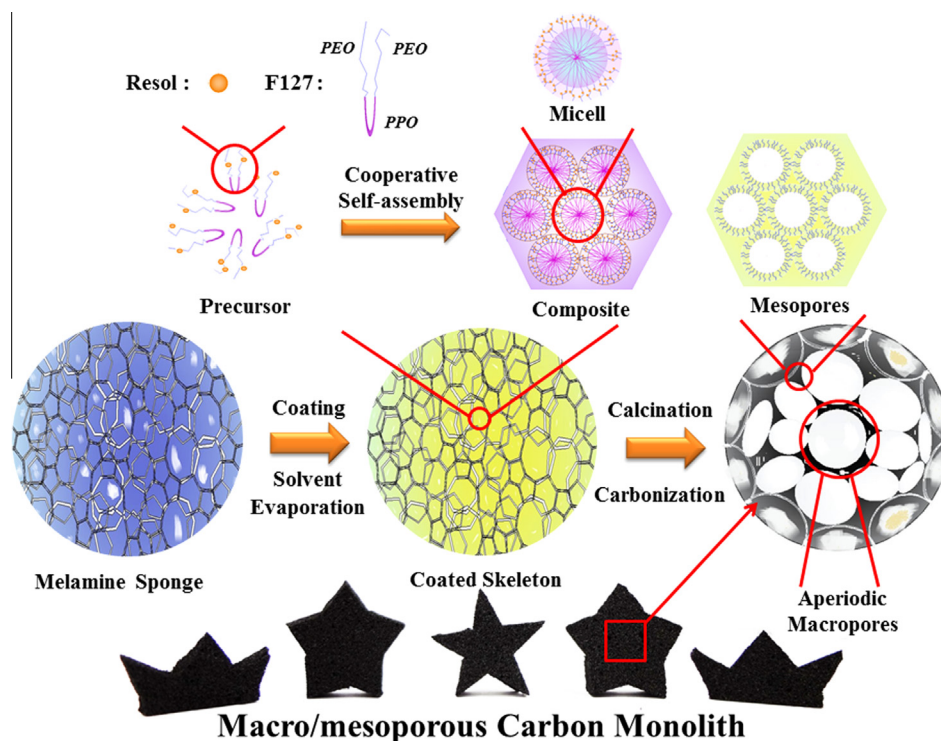


Fig. 1 – Schematic for the fabrication of macro/mesoporous carbon monolith. (A color version of this figure can be viewed online.)

## 2.2. Preparation of the macro/mesoporous carbon monolith

Soluble resol used as carbon source was prepared by a basic polymerization method described elsewhere in detail [17]. For a typical procedure, 10 g F127 copolymer was mixed with 85 g ethanol. The resulting solution was heated up to 40 °C to form a clear solution under stirring. 25 g resol alcoholic solution (40 wt%) was added in the above solution and kept stirring at room temperature over 6 h to obtain the precursor solution. 0.4 g of commercially available melamine sponge without any pretreatment was immersed into the above solution and sealed overnight. The above mixture was then exposed to air, and the spontaneous evaporation of solvent ensured the carbon precursor uniformly coated on the skeleton of the sponge. The block copolymer and resol aggregated and crosslinked into micell and resin, respectively. Composite was achieved by thermally curing of the coated skeleton at 100 °C for 24 h. The composite was then transferred to a tubular furnace for pyrolysis under a nitrogen flow and heated to 350, 600, and 1000 °C at 1 °C/min and held at these temperatures for 2 h, respectively. The resultant black carbon monolith was denoted as C-x, where x indicates the last pyrolysis temperature.

## 2.3. Characterization

The sponge morphology and carbon monolith microstructure were characterized by SEM (Hitachi S4800, Japan) and TEM (EOL JEM-2100, Japan). Thermal degradation behaviors of samples were conducted by thermo gravimetric analysis (BOIF WCT-II, China). Fourier transform infrared (FT-IR) spectra were collected on a Nexus spectrometer (Nicolet, USA) using KBr disk. N<sub>2</sub> sorption isotherms were measured at 77 K with an ASAP 2020 instrument (Micromeritics, USA). The specific surface area and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Contact angles of samples were performed on a DSA-100 contact-angle system (Kruss, Germany) at ambient temperature. The volumes of droplets were in the range of 7–9 μL.

## 2.4. Organic solvent and oil absorption tests of carbon monolith

The absorption capacities ( $q$ ) of the carbon monolith were measured on various organic solvents and oils. In a typical sorption test, certain carbon monolith ( $m_0$ ) was immersed into various organic liquids (ethanol, coal oil, diesel oil, paraffin oil, vegetable oil, peanut oil, castor oil) for 1 min, then took out and weighed ( $m_t$ ) quickly. The absorption measurements for all organic liquids were performed repeatedly five times. The  $q$  value was calculated according to the following equation:

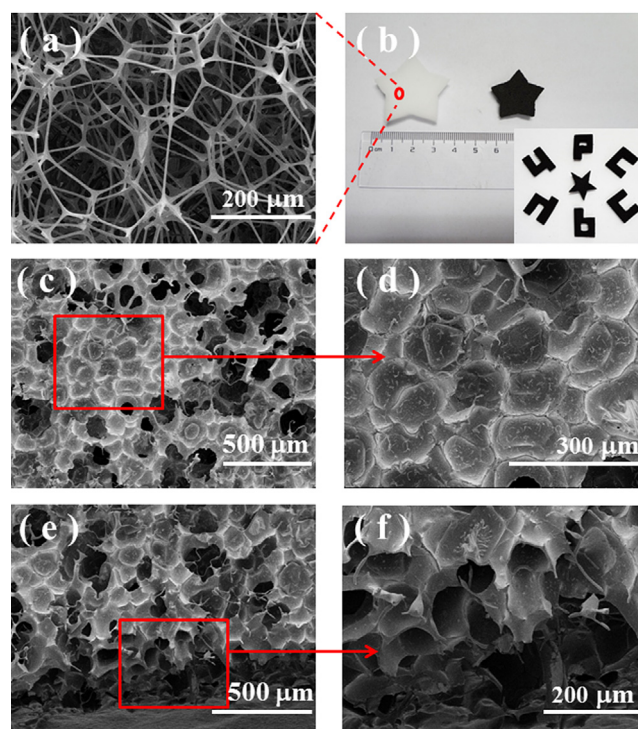
$$q = (m_t - m_0) / m_0 \times 100\%$$

The recyclability of carbon monolith was evaluated by the cyclic absorption-combustion measurement. Typically, the oil-fouled carbon monolith was directly combusted in air to remove absorbed oil, and then the oil-free sample was reused

in the next cycle. The weight of sample was recorded before and after each cycle to determine the recovery efficiency. Each organic liquid was tested five cycles.

## 3. Results and discussion

The SEM images of the raw melamine sponge and as-fabricated carbon monolith are shown in Fig. 2. The melamine sponge with a macroscopically rough surface is composed of macropores (80–160 μm in diameter), exhibiting a smooth reticular skeleton (Fig. 2a). After evaporation-induced self-assembly and coating process, the coated skeleton of sponge was pyrolyzed at different temperatures to fabricate carbon monolith. Fig. 2b displays the digital images of melamine sponge and carbon monolith pyrolyzed at 600 °C. Except for the volume shrinkage of the carbon monolith during the pyrolysis process, there is no apparent difference in their appearances and morphologies. More importantly, the carbon monolith with desired shape can be made by tailoring the initial shape of melamine sponge (see the inset in Fig. 2b). SEM image in Fig. 2c shows that the carbon monolith has an interconnected, aperiodic macroporous structure. At a higher magnification (Fig. 2d), irregular wrinkles are randomly distributed on the surface of blocked macropores. This special surface structure may be ascribed to the heterogeneous filling



**Fig. 2** – (a) SEM image of the raw melamine sponge. (b) Digital images of melamine sponge (left) and C-600 sample (right), the inset is a digital image of C-600 sample with different shapes. (c and d) SEM images of the top-view surface of C-600 sample at different magnifications. (e and f) SEM images of the cross-sectional morphology of C-600 sample at different magnifications. (A color version of this figure can be viewed online.)

of precursor on the sponge and the partial shrinkage of carbon monolith during the pyrolysis process. A cross-sectional view of carbon monolith in Fig. 2e exhibits a robust reticular skeleton. A high-magnification SEM image clearly shows that the macropores with a diameter of 70–150  $\mu\text{m}$  are highly interconnected with large numbers of junctions (Fig. 2f).

The TEM images of carbon monolith can clearly demonstrate the nano-scale structure, as shown in Fig. 3. The samples pyrolyzed at different temperatures, i.e. 350, 600 and 1000  $^{\circ}\text{C}$ , show well-ordered hexagonal arrays of mesopores with 1D channels, which can be well retained even after pyrolysis at 1000  $^{\circ}\text{C}$ , further confirming a 2D ordered hexagonal mesostructure [17]. The unit cell parameters of C-350, C-600 and C-1000 samples estimated from the TEM images are 12.6, 11.8 and 11.0 nm, respectively, indicating the highly stable mesostructure during the pyrolysis process. The HRTEM image (Fig. 3f) of C-1000 clearly exhibits the typical amorphous carbon structure, containing random graphitic striations in pore walls [18]. Therefore, through extensive SEM/TEM observations, the nano-scale ordered mesopores are successfully introduced into the micro-scale 3D robust reticular skeleton by a combination of evaporation-induced self-assembly and coating strategy, resulting hierarchical macro/mesoporous architecture.

Fig. 4 shows the nitrogen sorption isotherms and the corresponding pore size distribution of the carbon monoliths calcined at different temperatures. All samples have type-IV sorption isotherms, indicating the presence of uniform

mesopores with cylindrical channels [19]. The adsorption and desorption isotherms of C-350 are not closed, attributing to the sample's polymer framework [20]. The BET surface areas of C-350, C-600 and C-1000 are 309, 686 and 959  $\text{m}^2/\text{g}$ , respectively, and their corresponding total pore volumes are 0.45, 0.51 and 0.54  $\text{cm}^3/\text{g}$ . C-1000 calcined at the highest temperature exhibits the highest porosity. In comparison to C-350, C-600 and C-1000 samples have left-shift capillary condensation and wider pore size distribution, depending on the intensified asymmetric shrinkage and partial collapse at higher pyrolysis temperature. The mean pore sizes of C-350, C-600 and C-1000 are 7.5, 6.3 and 4.7 nm, respectively. The as-made macro/mesoporous carbon monoliths with high porosity are believed having superior absorption performance on oil–water separation.

The thermostability and decomposition behavior of materials were observed by the thermo gravimetric (TG) analysis, as shown in Fig. 5a. TG curve of resultant composite in nitrogen atmosphere shows that approximately 49 wt% weight loss occurred in the temperature range of 350–450  $^{\circ}\text{C}$ , corresponding to the partial decomposition of melamine sponge and block copolymer. Therefore, composite pyrolyzed at as low as 350  $^{\circ}\text{C}$  can remove skeleton structure to fabricate hierarchical porous structure. Subsequently, a continuous slower weight loss of composite occurs in the range of 450–800  $^{\circ}\text{C}$ , which is similar to the degradation behavior of phenolic resin. With good thermostability and high carbon content, phenolic resin can act as skeleton to support the hierarchical porous

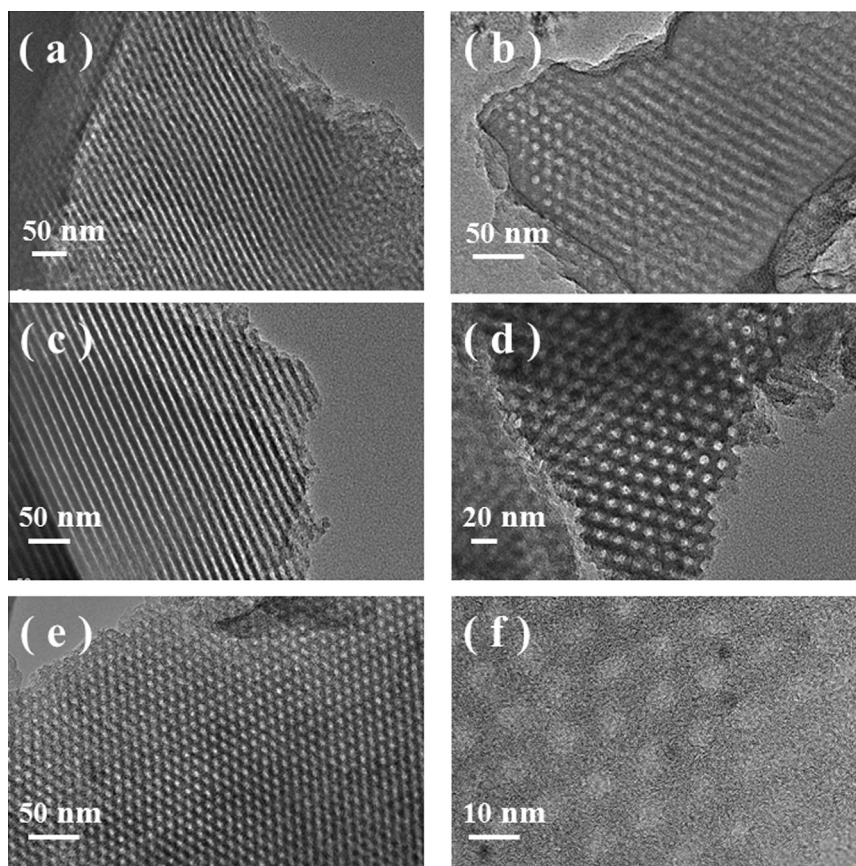
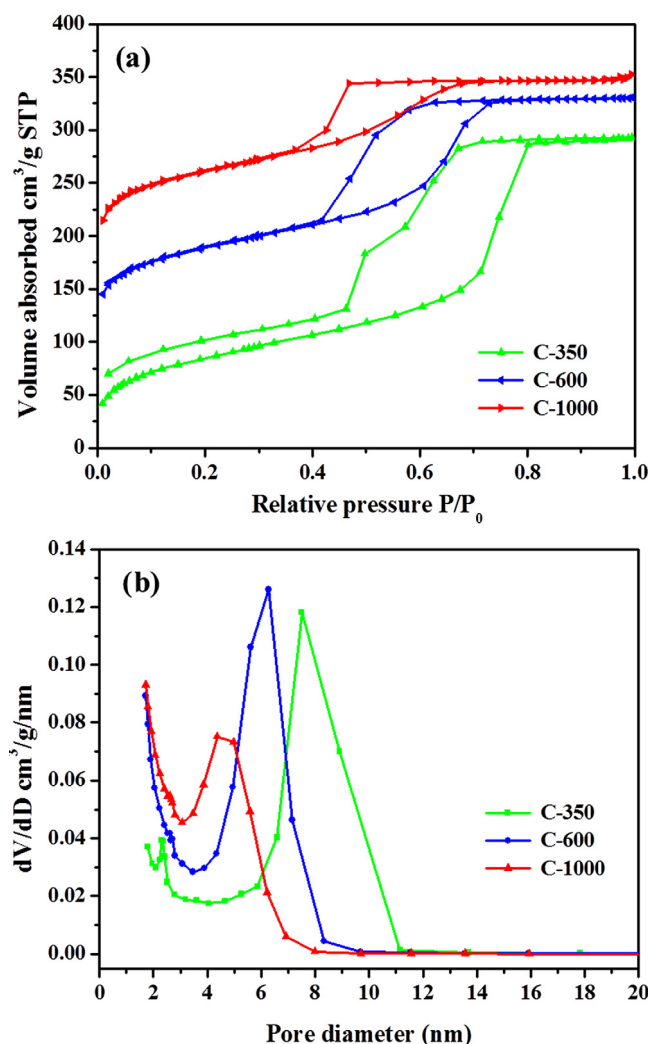


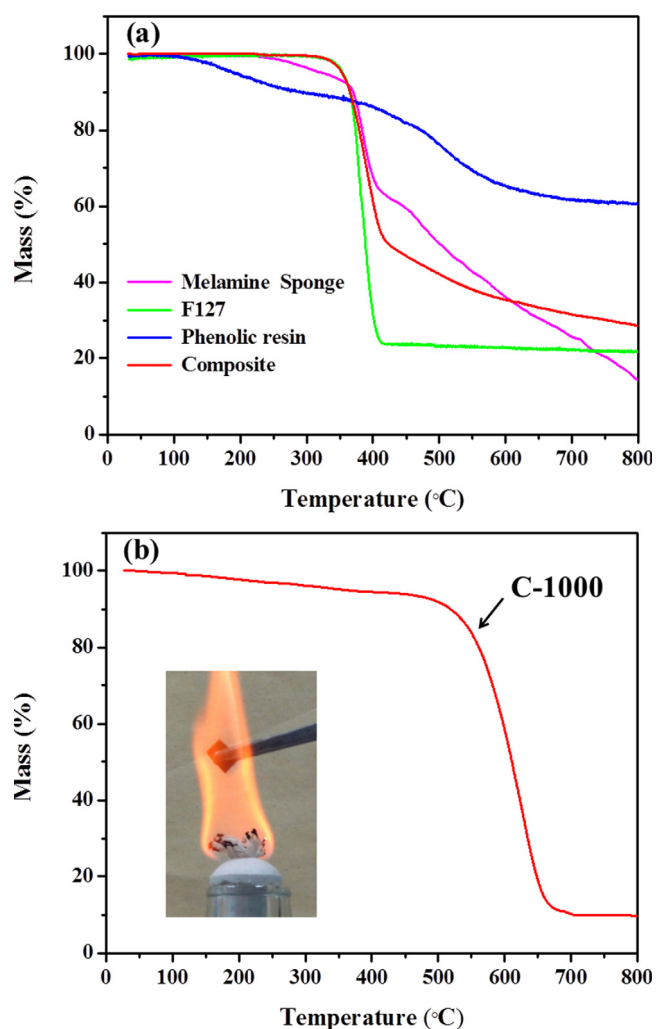
Fig. 3 – TEM images of C-350 (a and b), C-600 (c and d), and C-1000 (e) samples. HRTEM image of the C-1000 sample (f).



**Fig. 4** – (a) N<sub>2</sub> adsorption–desorption isotherms and (b) corresponding pore size distribution plots of the carbon monoliths pyrolyzed at different temperatures. (A color version of this figure can be viewed online.)

structure, and finally convert into carbonaceous components of macro/mesoporous monolith. Meanwhile, the decomposition behavior of carbon monolith in air is shown in Fig. 5b. The weight loss of C-1000 sample is only 8 wt% at 500 °C, mainly resulting from the removal of water adsorbed on porous structure as well as the destruction of labile oxygen-containing functional groups in the sample [21]. Therefore, when C-1000 sample is exposed to the flame of alcohol burner, it can keep from combustion and remain inert, suggesting superior fire-resistant property (see the inset in Fig. 5b and Movie S1).

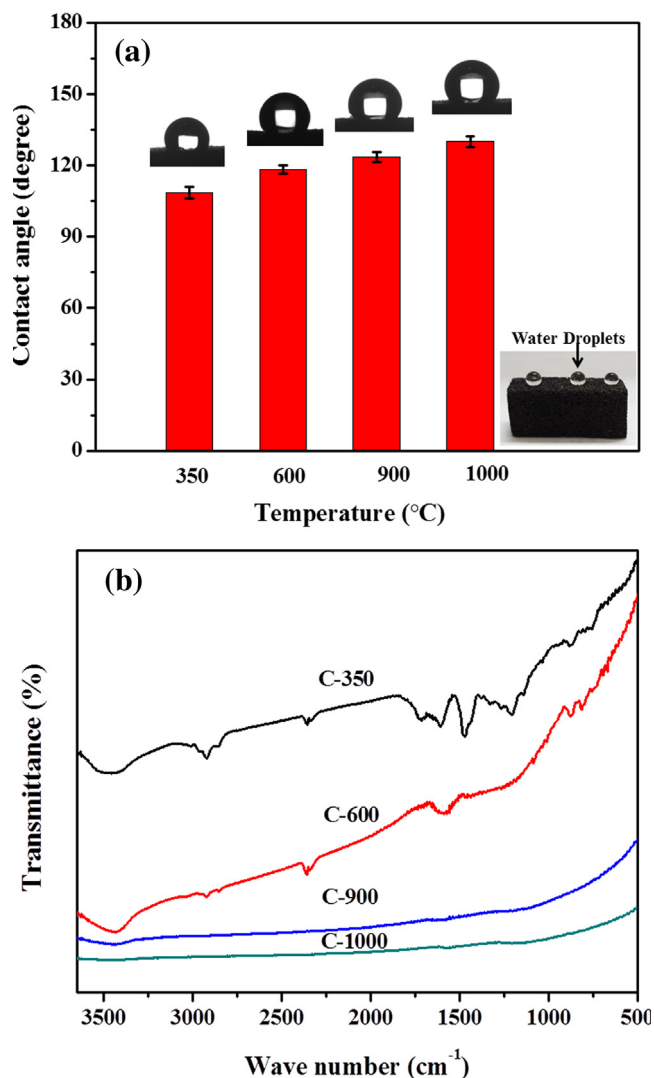
The wettability of as-made macro/mesoporous monolith is a crucial factor for oil–water separation. The as-fabricated carbon monolith can support quasi-spherical water droplets on its surface (the inset in Fig. 6a). Benefited from the micro/nano-scale structure, the carbon monolith dramatically increases the surface roughness, which is close to the surface structure of a lotus leaf, therefore possessing hydrophobic property [22]. It is well-known that the pyrolysis temperature



**Fig. 5** – (a) TG curves of melamine sponge, F127, phenolic resin, and resultant composite in nitrogen atmosphere. (b) TG curve of C-1000 in air atmosphere, the inset is a photograph of C-1000 in a flame of an alcohol burner. (A color version of this figure can be viewed online.)

has a great influence on the resultant carbon monoliths [17]. The water contact angles of carbon monoliths are in the range of 108.6–130.0°, increasing with the rising pyrolysis temperature (Fig. 6a). These differences in the wettability of carbon monoliths pyrolyzed at different temperatures can also be explained by FT-IR spectroscopy analysis (Fig. 6b). The FT-IR spectrum of C-350 sample shows several peaks of hydrophilic functional groups, such as C=O, C–O, and –OH, while C-600 sample reveals relatively weak hydrophilic peaks. For C-1000 sample, no functional groups are observed. As a result, C-1000 sample has the largest water contact angle, which means the highest hydrophobicity.

Furthermore, the wetting behaviors of water and oil on the carbon monolith surface are characterized in more detail. The underwater oil wettability was examined by immersing the carbon monolith in aqueous solution. When C-1000 sample floated on the water surface due to its hydrophobicity and low weight, the carbon monolith had a contact angle of almost 0° for coal oil droplet in water, and



**Fig. 6 – (a) Water contact angle measurements of carbon monoliths at different pyrolysis temperatures, the inset is a photograph of water droplets on the surface of C-1000. (b) FT-IR spectra of carbon monoliths at different pyrolysis temperatures. (A color version of this figure can be viewed online.)**

coal oil was absorbed quickly by carbon monolith (Fig. 7a and Movie S2). This can be ascribed to the high porosity and superoleophilicity of carbon monolith, which can induce superwetting capillary action for oil, leading to an immediate spreading and permeating behavior of oil on carbon monolith [23]. However, when C-1000 sample was submerged in coal oil by an external force, the carbon monolith also presented a highly hydrophobicity (Fig. 7b and Movie S3). The under-oil water droplet can keep quasi-spherical shape on the surface of C-1000 with  $146^\circ$  of water contact angle. The particular wettability achieved in oil/water/solid three-phase system may be mainly attributed to the multi-scale surface structure of the carbon monolith, in which those trapped oil molecules can greatly reduce the contact area between water and carbon monolith surface, leading to a large water contact angle under oil [24].

The hierarchical macro/mesoporous carbon monolith with high porosity, good hydrophobicity, and intrinsic fire-resistant property, can be used as a sorbent for the removal of organic solvents and oils from water. The oil–water separation experiment was carried out in a simple setup, as shown in Fig. 8 and Movie S4. Here, we chose C-1000 sample as a sorbent to demonstrate the absorption capacity of the carbon monolith. When a small piece of C-1000 sample was forced to the paraffin oil (dyed with oil paint) on a water surface, it absorbed the paraffin oil completely and rapidly, resulting in the clean water initially contaminated by the paraffin oil. Moreover, the C-1000 fouled by paraffin oil was separated entirely from the water simply by taking it out without leakage of paraffin oil, exhibiting excellent oil-keeping performance and providing a facile and useful route for cleaning up oil spillage and organic compound leakage.

Furthermore, in order to evaluate the absorption capacity ( $q$ ) for organic solvents and oils, absorption tests were performed in various kinds of organic liquids without water environment, such as the commercial petroleum products (coal oil, diesel oil, paraffin oil), fats (vegetable oil, peanut oil) and organic solvents (ethanol). These organic liquids are common contaminants in our daily life or industry. The  $q$  values show that the absorption capacities of C-1000 sample for the aforementioned organic liquids are all over 89 wt% and reach a maximum of 203 wt% for peanut oil (Fig. 9a). However, comparing to the C-1000, C-600 sample has lower  $q$  values ranged from 61 to 99 wt% for various organic liquids. The differences in  $q$  values can be attributed to the differences in the pore structure parameters of carbon monoliths. The oil absorbed mechanism is mainly physical absorption of organic molecules, which can be stored in the pores of materials [25]. Due to the higher porosity of C-1000 than that of C-600, C-1000 can absorb more organic molecules and store in its hierarchical porous structure.

For both C-600 and C-1000 samples, the absorption capacities for all organic liquids are almost in the same order (Fig. 9a): ethanol  $\leq$  coal oil  $<$  diesel oil  $<$  paraffin oil  $<$  vegetable oil  $\leq$  peanut oil  $<$  castor oil, which corresponds to the increasing density of organic liquids. To further confirm these trends, we investigated the relationship between densities of various organic liquids and absorption capacity of C-1000 sample. It can be found that organic liquid with higher density has a larger  $q$  value (Fig. 9b). It has been reported that the absorption capacity is dependent on the void volume of the porous materials [26]. Therefore, when the void volume of materials is fixed, the organic liquid absorbed on the void is also fixed, thereby leading to the obvious linear correlation between the absorption capacity and the density of organic liquid.

The recyclability of sorbents has also become an important criterion for oil spill cleanup applications. Benefited from the intrinsic fire-resistant property of macro/mesoporous carbon monolith, direct combustion of the oil-fouled carbon monolith in air can effectively regenerate the carbon monolith. Thus, the recyclability tests are performed from various organic liquids to evaluate the regeneration capacity of as-made carbon monolith (Fig. 10). For example, C-1000 sample fouled with ethanol was burned for recycle use, and no structural damage was found on C-1000 (the inset in Fig. 10 and

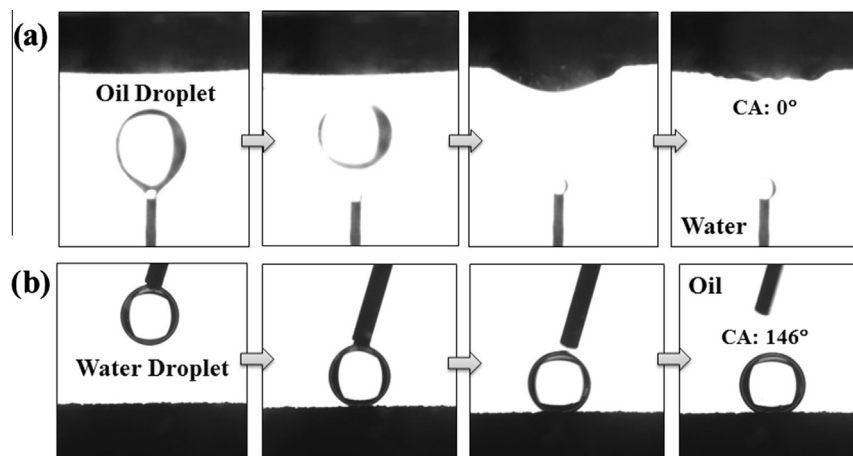


Fig. 7 – (a) Optical images of the dynamic spreading process of coal oil droplet towards C-1000 sample in water. (b) Wetting behavior of water droplet on the surface of C-1000 sample in coal oil.

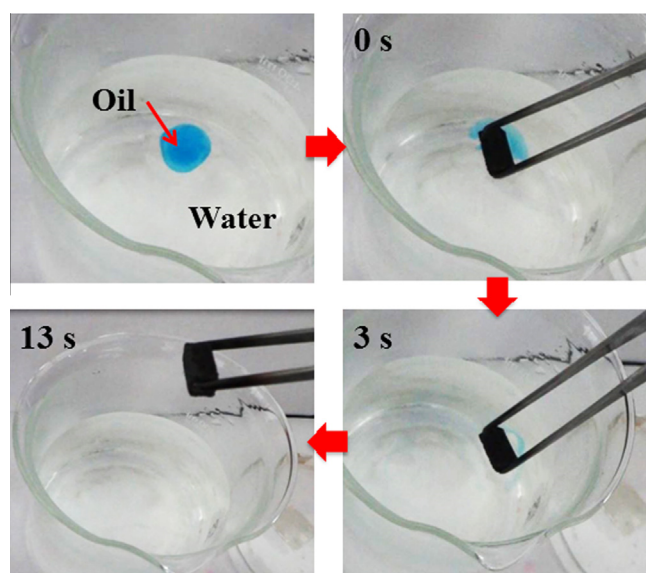


Fig. 8 – Photographs of the removal process of paraffin oil from water using C-1000 sample, paraffin oil dyed with oil paint to facilitate clear observation of the phenomenon. (A color version of this figure can be viewed online.)

[Movie S5](#)). After five absorption-combustion cycles, the standard deviation of absorption capacity maintained almost 5.5 wt% for all organic liquids, and less than 1 wt% of residual weight remained in C-1000 sample after each cycle, indicating a relatively stable recyclable performance of as-made carbon monolith. The slightly change of the absorption capacity for each cycle may be ascribed to the residual weight of organic liquid remained in C-1000 sample during incomplete combustion process. The results clearly suggest the excellent recyclability of the carbon monolith when used as a sorbent for oil-water separation. [Table S1](#) shows the comparison of macro/mesoporous carbon monolith with several typical carbon-based sorbents reported before. Although the absorption capacity of the resultant macro/mesoporous carbon monolith is still lower than those of graphene sponge, carbon

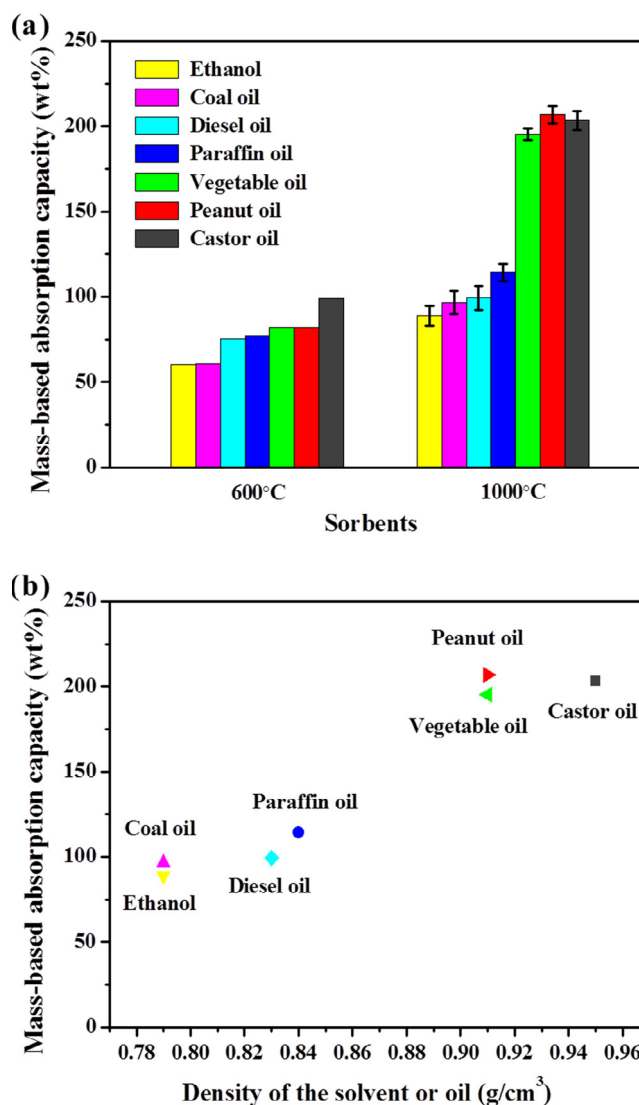
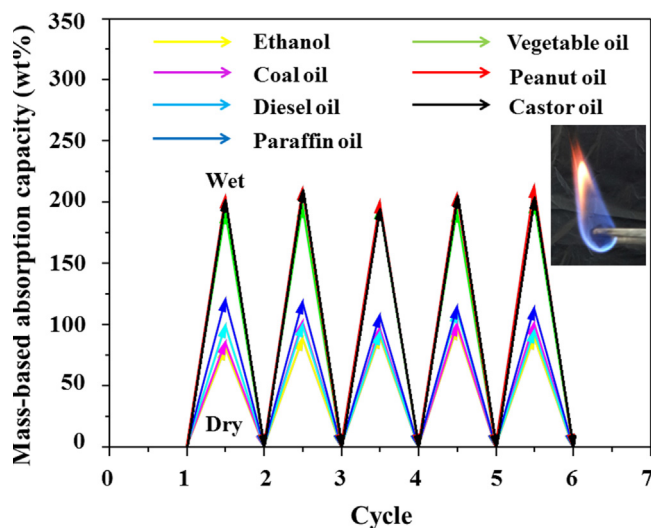


Fig. 9 – (a) Absorption capacities of C-600 and C-1000 samples for various organic liquids. (b) The relationship between the density of organic liquids and the absorption capacity of C-1000 sample. (A color version of this figure can be viewed online.)



**Fig. 10 – Cyclic sorption of various organic liquids in C-1000 sample, the inset is a photograph of the combustion of C-1000 fouled with ethanol. (A color version of this figure can be viewed online.)**

nanotube, carbonaceous fiber and graphene microsphere [27–32], the former has special outstanding features including low-cost and available raw materials, good recyclability, as well as simple fabrication method. Most importantly, the mass production of the macro/mesoporous carbon monolith has practical applications.

#### 4. Conclusions

We demonstrate a facile strategy to fabricate hierarchical macro/mesoporous carbon monolith from cheap melamine sponge by a simple evaporation-induced self-assembly and coating method. The melamine sponge with micro-scale 3D reticular skeleton provides an interface for the cooperative self-assembly and coating of the block copolymer and resol. Benefited from solvent evaporation and pyrolysis process, the nano-scale ordered mesopores can be successfully introduced into the macroporous system. Depending on the rough surface caused by micro/nano-scale porous architecture, the resultant carbon monolith exhibits high porosity and excellent hydrophobicity. When used as a sorbent for oil–water separation, the carbon monolith can effectively and selectively absorb oil from water. In addition, coupling with the intrinsic fire-resistant property, the oil-fouled carbon monolith can be direct burned in air without any structure destruction, exhibiting good recyclability. More importantly, the low-cost and available source, and the simple preparation method make the carbon monolith easy to be scaled up for potential industry applications. Therefore, the macro/mesoporous carbon monolith offers a new avenue as a versatile, efficient, and safe sorbent in the field of oil spill cleanup.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2014.12.055>.

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