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Bio-inspired modification of silicon carbide foams for oil/water separation and rapid power-free absorption towards highly viscous oils

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Abstract

A bio-inspired strategy for the fabrication of superhydrophobic silicon carbide (SiC) ceramic foams (SCFs) using commercially available melamine foam (MF) as the template and vinyl-containing hyperbranched liquid polycarbosilane (VHPCS) as the binder was developed. The pre-oxidation process and crystallization degree during the sintering were monitored by Fourier transform infrared spectroscopy and X-ray diffraction. A plausible reaction was proposed and the thermogravimetry analysis results indicated that VHPCS was more suitable for the adhesive agent of SiC powders. By optimizing the mass ratio of VHPCS and SiC, a maximum compression

strength of 1.25 MPa for SCFs was achieved with a low density of 0.514 g/cm^3 and only 6.72% of volume shrinkage. The obtained SCFs exhibited rapid power-free absorption towards highly viscous oils after a biomimetic surface modification with n-octadecylamine (ODA). It took only 22 seconds for the complete absorption of $200 \mu\text{L}$ ultra-high viscosity oil (5000 mPa s). A probable mechanism for the rapid absorption of viscous oil had been revealed and the decoration of low-surface-energy molecules together with the distinct porous structure were regarded as the critical factors.

Graphical abstract

A bio-inspired strategy was applied for the surface modification of silicon carbide foams with rapid power-free absorption capacity towards ultra-high viscosity oils.

Keywords: Bio-inspired; Power-free; Silicon carbide foams; Ultra-high viscosity oil

1. Introduction

With the rapid development of the offshore oil industry and the frequent oil-spill accidents that follow, various types of pollution caused by crude oil, petroleum products and toxic organic solvents have become severe threats to the ocean ecosystem. An efficient, energy and cost-effective method for the clean-up of oily contaminants, especially for the oils with high viscosity, is highly desired yet still a global challenge in practical applications. Although many traditional methods, such as air flotation, controlling combustion, centrifuges, oil skimmers, dispersants and solidifiers, have been exploited for the clean-up of oily pollution's references, they still cannot meet all the criteria summarized by previous works, mainly due to their drawbacks of time-consuming, inefficiency, environmental unfriendly, or even toxicity [1-3].

Recently, the advanced 3D sorbents have drawn increasing attention because of their light weight, large surface area as well as feasible surface modification [4-6]. In principle, as a sort of typical oil sorbent, 3D porous materials with superhydrophobic/oleophilic surface exhibited great potential to realize the function of oil/water separation in an effective and facile way, because of their intrinsic different wettability of water and oil. Therefore, various hydrophobic 3D materials in forms of sponge, aerogel and foam were synthesized [7-10]. Many works have confirmed that 3D materials possess the excellent ability of oil/water separation. Nevertheless, the oil-spill remediation for the heavy crude oils is still a huge problem because of their low capture performance. Most of these previous cases involved in

oil/water separation were focused on the low-viscosity oils. For example, Zha *et al.* prepared the hybrid PVDF/graphene gel by the diffusion of nonsolvent (methanol or water) into PVDF/graphene suspension in N, N-dimethylformamide (DMF) [11]. In addition to polymer-based composites, 3D gels consist of carbon materials were also confirmed to be suitable oil absorbents [12-14]. Bi *et al.* produced the aerogels made from twisted carbon fibers to absorb the organic solvents and oils [15]. With regard to the motion of viscous liquid in the 3D porous media, the classical Darcy's law was used to describe the seepage velocity (v) as (equation 1)

$$v = -\frac{K}{\mu} \frac{dp}{dL} \quad (1)$$

Where k is the hydraulic conductivity; p represents the pressure; L for the path length; μ is the viscosity [16]. As can be seen from the above formula, the higher the viscosity of liquid, the slower the penetration rate would appear. Recently, Yu *et al.* prepared graphene coated melamine foam (MF) for the highly viscous oil via a Joule-heat process [2]. A dramatically improved oil-absorption rate was reported as the oil viscosity decreased rapidly with increased temperature. However, the undesired rapid heat dissipation into the environment from the graphene-wrapped sponge could raise a concern on energy efficiency [17].

One more step further, the absorption of highly viscous oil without extra heating would be much more interesting and desirable. Ceramic foam, which is chemically inert, compressive and thermostable, has long been considered as fundamental materials in many engineering applications [18-22]. The relatively large specific surface area and the diverse-roughness surface of SiC foam make it has good

absorption kinetics in the absorption process, which can reach the absorption equilibrium faster, and its macro-porous structure and micro-pore can be used as oil storage space, so it is promising to be used as a potential material for oil absorption. For the preparation of SCF, many strategies have been adopted to aid the formation of a cellular structure, such as the addition of chemical foaming agents [23], the sol-gel process [24-26], or the usage of three-dimensional porous templates [27,28]. By contrast, the great advantages of template-based methods are that they are high efficiency, easy to be operated and facile to adjust the honeycomb morphologies. Melamine foam (MF) is a kind of typical polymer foam with a three-dimensional grid structure and a high opening ratio of more than 99%, making it an ideal template for fabricating SiC foam. In a typical process for the preparation of impregnation slurry, SiC powders are usually used as the skeleton material. Nevertheless, it is hard to obtain an integrated SCF without the addition of a suitable binder. Recently, a vinyl-containing liquid polycarbosilane (VHPCS) with hyperbranched molecular structure has attracted wide interest due to its good flowability, self-crosslinking and high ceramic yield.

Herein, we reported one type of silicon carbide foams (SCFs) fabricated by the impregnation of MF with organic slurry consisting of VHPCS and SiC powders, followed by a thermal oxidation treatment and pyrolysis process in an inert atmosphere. Hyperbranched VHPCS used here is the binder agent for silicon carbide (SiC) powders. Inspired by a biomimetic approach, *n*-octadecylamine (ODA) with long alkyl chains were decorated onto SCFs via a Schiff base reaction and Michael

addition, endowing SCFs a superhydrophobic/oleophilic surface. The optimized preoxidation mechanism together with a ceramic yield of VHPCS, porous structure and compression strength of SiC foams were investigated. Most importantly, the obtained SiC foams were confirmed to be an ideal candidate for oil/water separation and exhibited high-performance absorption ability, especially for those oils with high viscosity.

2. Experimental

2.1. Materials

Melamine foams were manufactured by KELINMEI and used as foam skeleton; Vinyl-containing liquid polycarbosilane (VHPCS) with a highly branched structure (provided by Institute of Chemistry, Chinese Academy of Sciences); SiC powders (0.5~10 μm), *n*-hexane (95%), 3-hydroxytyramine hydrochloride (dopamine, 98%) and tris-(hydroxy-methyl) aminomethane (TRIS, 99%, a buffer agent) were purchased from Sigma-Aldrich; Dicumyl peroxide (DCP) and *n*-octadecylamine (ODA) were purchased from Aladdin Reagent Corp. (Shanghai, China). Oil Red O, methyl blue powders, dimethyl silicone, dibromoethane and ethanol were commercially available from Shanghai Mclean Biochemical Technology Co., Ltd. Deionized water were home-made in our group. Polycarbosilane (PCS) was provided by Cerafil Company in Suzhou, China. All chemical reagents and solvents were used as received and without further purification.

2.2. Preparation of SiC ceramic foams (SCFs)

The fabrication process for the preparation of SCFs is illustrated in Fig. 1. A

piece of melamine foam with open-cells of size 50-100 μm was used in this study. The SiC powder with an average particle size of 5 μm was mixed with VHPCS at a certain ratio (1: 9, 3: 7, 1: 1, 7: 3, 9: 1) and dissolved in *n*-hexane solution to form a slurry. Then, DCP (0.3% by mass of VHPCS) was added as an initiator. Meanwhile, the MF was cut into a cube with a size of 20 mm $\times$ 20 mm $\times$ 20 mm. And then the cube was immersed in the slurry for about 120 minutes. The samples were allowed to dry at room temperature for 24 hours and cured at 220 $^{\circ}\text{C}$ in air to obtain a pre-oxidized foam.

Fig. 1. Schematic illustration for the preparation of SiC foams.

The SCFs were obtained by placing the pre-oxidized foam in a high-temperature tube furnace heated to 1250 $^{\circ}\text{C}$ under nitrogen atmosphere, with a heating ramp of 10 $^{\circ}\text{C}/\text{min}$ and then cooling in the furnace to ambient temperature. A flow of nitrogen was used during 20 min before the pyrolysis to ensure a neutral atmosphere. The final obtained SCFs were referred as 1-9-SCF, 3-7-SCF, 1-1-SCF, 7-3-SCF and 9-1-SCF, according to the mass ratio between SiC and VHPCS.

2.3. Preparation of hydrophilic SCFs

In a typical synthesis method for the polydopamine-coated ceramic foams, SCFs were firstly immersed in 100 mL buffer solution (10 mM, pH=8.5) followed by the addition of 270 mg dopamine. After a bath sonication for 10 min, the mixture was then put under magnetic stirring at room temperature for 24 h. The PDA-coated SCFs (SCF-PDA) were collected via a water-washing treatment before being dried in a vacuum oven at 50 °C for 24 h.

Afterwards, SCF-PDA was allowed to react with ODA through amine-catechol adduct formation. Briefly, SCF-PDA were immersed in 100 mL ethanol with a concentration of 20 mM ODA and then stirred for 24 h. After being rinsed thoroughly with ethanol to remove unreacted ODA, the ODA-functionalized SCFs (SCF-ODA) were dried at 50 °C under a vacuum for 24 h.

2.4. Characterizations

The pyrolytic yields of PCS and VHPCS precursor were measured by thermogravimetric analyzer (TGA, Setsys Evolution, France) with a heating rate of 10 °C/min from ambient temperature to 900 °C in N₂. Fourier Transform Infrared spectra (FTIR, Nicolet iS50, America) were collected in the range of 400-4000 cm⁻¹. The crystallization of MF, VHPCS and SCFs pyrolyzed at 1250 °C in nitrogen were characterized by X-ray diffraction (XRD) with a brand of D8 Advance/Bruker produced in Germany. The voltage and current settings of the diffractometer were 40 kV and 30 mA, respectively. The scan range was from 10 to 90° with a step size of 0.05° and a scan speed of 0.0258 s. The structural features of all types of foams were investigated using a scanning electron microscope (SEM, JSM-6490LV/JEOL). Water

contact angle measurements were carried out on an Optima goniometer (DSAHT, Germany) to evaluate the surface wetting of SCFs. The compressive mechanical tests were performed by an electronic universal testing machine (WSM-20KN, China), with two parallel flat-surfaces and a 200 N detection cell moving at a speed of 2 mm/min.

3. Results and discussion

3.1. Preparation of SCFs

Before the sintering treatment, a curing step was performed at 160, 220 and 250 °C. The collected FTIR data were shown in Fig. 2a, two peaks at 2100 and 935 cm^{-1} ascribed to the stretching and bending vibration of Si-H became weaker when compared to as-received VHPCS, implying curing reactions occurred. The possible reactions were proposed in Fig. 2b. The transformation of Si-H to Si-OH and further to Si-O-Si was confirmed by the peaks of -OH and Si-O-Si located at 3400 and 1128 cm^{-1} , respectively. The peak at 840 cm^{-1} corresponding to Si-C bonding attenuated with the increased curing temperature, consolidating the reaction between Si-H and Si-CH₃ (Fig. 2b). Higher ceramic yield not only benefits for improving binding effect but also preventing the dramatic volume shrinkage during the formation of ceramic foams. Herein, liquid-state VHPCS exhibited obviously higher ceramic yield as compared to the solid polycarbosilane (PCS). According to the TGA curves in Fig. 2c, an obviously increased ceramic yield of VHPCS (81.86 wt. %) was recorded as compared to that of PCS (49.17 wt. %).

The XRD patterns of the MF, VHPCS, MF impregnated with VHPCS

(MF-VHPCS) and MF impregnated with the mixture of VHPCS and β -SiC powders (MF-VHPCS-SiC) after sintering at 1250 °C were presented in Fig. 2d. In the case of MF, a broad diffraction peak at 20-30° was assigned to the amorphous carbon. While for the VHPCS and MF-VHPCS, three broad peaks at 35.6°, 60° and 71.8° correspond to the (111), (220) and (311) planes of β -SiC, respectively, implying the formed SiC is not fully crystallized at 1250 °C [29]. By comparison, the peaks of β -SiC in MF-VHPCS-SiC were very sharp at the temperature of 1250 °C, as a result of the high crystallinity. It is interesting to notice that two weak peaks from carbon appeared in XRD patterns of MF-VHPCS-SiC. The carbon may be due to the existence of the excessive carbon of the sintered MF.

Fig. 2. (a) FT-IR spectra of VHPCS and pre-oxidized VHPCS; (b) proposed chemical reactions of VHPCS; (c) TGA curves of VHPCS and PCS; (d) XRD pattern of MF,

VHPCS, MF-VHPCS and MF-VHPCS-SiC.

3.2 Mechanical properties

Mechanical property is an important issue for the practical application of hierarchical porous materials. As reflected in Fig. 3, we further investigated the compression strength, volume shrinkage and micro-morphologies of SCFs with different compositions. The strength values of SCFs were depicted in Fig. 3a. Benchmarked against the light weight existing foams with density values of $\rho = 0.391 \sim 0.514 \text{ g/cm}^3$, we found that our foams possess higher compression strengths when compared to the values reported in the literatures (Table 1) [30-33]. The composition of slurry is an important factor affecting the mechanical properties of silicon carbide foams. As the results revealed, the resulting SiC foams exhibit both high compression strengths and specific compression strength. The maximum compression strength of those SiC foams was 1.25 MPa for the SCF in which the mass ratio of VHPCS to SiC was 1:1, which also showed a low density of 0.514 g/cm^3 with a high porosity of 84%. When the mass ratio of VHPCS to SiC was 1:9, the minimum point of compression strength appeared on the curve. This may be due to the excessive SiC which deteriorates the fluidity of the slurry seriously, resulting in an incomplete infiltration during the soaking treatment of MF. Also, during the extrusion process, the slurry may be pulverized on the skeleton of MF after the evaporation of the solvent, because too many SiC powders left on the skeleton. In addition, we find that the mechanical properties of the foam decrease significantly when the mass ratio of VHPCS to SiC was 9:1. This is because the lower the solid content of the slurry, the farther the

distance between the ceramic particles, making it difficult to form the dense structure.

In a word, the obtained SCFs with higher VHPCS or SiC content possessed the obviously weaker capability of pressure resistance. The strength of the foam walls, affected by the binding force between the SiC powders, is believed to determine the mechanical strength of 3D ceramic foams to a large extent. Since the serious shrinkage would occur in the sintering treatment of the VHPCS-SiC slurry, the subsequent micro-morphologies and defects formed in the SCFs would affect the strength of the foam wall obviously. Actually, the volume shrinkage as a function of VHPCS/SiC ratio varied in the same tendency when compared to the compression strength, suggesting a more stable structure formed in the SCF with 50 wt. % VHPCS (Fig. 3b).

Fig. 3. Compression strength (a) and volume shrinkage (b) of SCFs; SEM images of 1-9-SCF (c), 1-1-SCF (d), 9-1-SCF (e).

Table 1. Summarized compression strength data of SiC foams in literatures

Materials	Density (g/cm ³)	Compression strength (MPa)	Specific compression strength (MPa cm ³ g ⁻¹)	Ref.
SiO ₂ , Graphene foam	0.017	0.035	2.059	[30]
Sucrose, Silicon powders	0.168	0.160	0.952	[31]
Sucrose, Silicon powders	0.227	0.410	1.809	[31]
Silicon powders, Magnesium Nitrate	0.115	0.240	2.087	[32]
PU foam, Allylhydropolycarbosilane	0.350	0.750	2.143	[33]
MF, SiC powders, VHPCS	0.391	0.890	2.276	This study
MF, SiC Powders, VHPCS	0.514	1.250	2.432	This study

Furthermore, the SEM images (Fig. 3c-e) were collected to characterize the micro-structure of SCFs. It can be found that the use of an appropriate amount of VHPCS is particularly important for the mechanical properties of SCFs. As can be seen in Fig. 3c, due to the release of many vapor molecules during the pyrolysis of VHPCS, serious cracks and discontinuous structure can form in the SCF made of 90 wt.% VHPCS, leading to a worse mechanical strength. Conversely, in Fig. 3c, the SCF was prepared with only 10 wt. % VHPCS, so that many individual SiC particles were randomly stacked to form a loose structure. Owing to the lack of VHPCS that can act as an effective adhesive agent for SiC particles, the binding force between those SiC particles became quite weak. Therefore, the SCF exhibit very poor anti-compression capability. In fact, the different mechanical properties of SCFs are also reflected in their digital photos. It is very hard to obtain integrated cubic samples for those SCFs fabricated with too much or too less VHPCS. Our results showed that 50 wt. % VHPCS is the optimized dosage for the fabrication of SCF in current work.

3.3 Surface modification of SCFs

In principle, the ideal candidates for oil/water separation should be both hydrophobic and oleophilic, which can be achieved by a certain roughness (classical

micro-nano hierarchical structure) with low surface energy materials [5,34]. But, it is not easy to achieve surface modification on SCFs because of the chemical inert of ceramic foams. To endow the ceramic foams with superhydrophobicity, a bio-inspired surface grafting strategy was applied. Many previous works have demonstrated that the dopamine containing *L*-DOPA and lysine inspired by the mussel protein adhesive could self-polymerize and adhere to almost all types of substrates [35, 36]. And, the mussels can be stably attached to the reefs in a very tough environment. (Fig. 4a). Therefore, in this work, by virtue of the polymerization of dopamine, ODA with long alkyl chain was successfully grafted onto the surface of SiC foams via the typical Schiff base reaction and Michael addition.

Fig. 4. (a) Image of the mussels adhered on the rock; (b) Schematic description of procedures for the preparation of the superhydrophobic SiC foam; (c) Reaction mechanism of dopamine and ODA during the dip-coating process; (d) pure SiC foam skeleton; (e) SiC foam skeleton modified with polydopamine and the contact angle of SCF-ODA; (f) FTIR spectra of SiC foam, SCF-PDA, SCF-ODA and ODA.

The process schematic of surface modification and detailed reaction procedures were illustrated in Fig. 4b and 4c. To activate the inert surface of SCF, the as-prepared SiC foam (defined as SCF-AR) was firstly soaked in a buffer solution of dopamine (pH = 8.5). The catechol groups of dopamine in the weakly alkaline solution will be oxidized to benzoquinone, and then transfer to 5,6-dihydroxyindole or further to 5,6-indolequinone via a nucleophilic reaction and rearrangement, resulting in a self-assembled PDA layer coated on the matrix by irreversible covalent bonds [37, 38]. As a consequence, the obtained SiC foam (SCF-PDA) was coated with a layer of PDA film, leading to the formation of functionalized surface with plenty functional groups.

Subsequently, SCF-PDA was immersed into ODA solution to complete surface treatment. By a typical Michael addition or Schiff base reaction between amino and quinone groups, as shown in Fig. 4c, ODA was grafted onto SCF-PDA. The morphology change for SCF-AR and SCF-ODA were shown in Fig. 4d and 4e. Before the surface treatment, the SCF-AR skeleton was relatively smooth except for some inconspicuous grooves. By comparison, the surface of SCF-ODA skeleton was uneven and some embossments with different sizes of 400-800 nm can be clearly observed. As expected, the superhydrophobic surface was demonstrated because a

contact angle of 153° was observed in the case of SCF-ODA as shown in Fig. 4e. Besides, a direct evidence for the successful surface functionalization of SCFs was provided by FTIR spectra shown in Fig. 4f. For the SCF-ODA, the peaks at 2922 and 2854 cm^{-1} associated with C–H stretching vibration became distinct, contributed by the rich methyl and methylene groups of grafted ODA molecules. Especially the new absorption peak in SCF-ODA appeared at 720 cm^{-1} is the characteristic absorption peak belonging to long-chain-paraffin.

3.4 Oil/water separation

As compared to SCF, the porous structure of SCF-ODA (in Fig. S1) was maintained, which is of great importance to the subsequent absorption tests. In Fig. 5, a drop of oil (red) and water was separately dropped onto the SCF-AR. We found oil absorption is very slow while the water droplet was absorbed immediately once it contacted the ceramic foam (Fig. 5a), indicating that the raw SiC foams were not suitable for the oil/water separation. Thus, it is inferred that the hierarchical structure formed in the SCF-AR cannot guarantee an effective oil/water separation. Fig. 5b displayed that a spherical water droplet can be formed on the surface of SCF-ODA while the red oil droplet was completely absorbed, manifesting a hydrophobic and oleophilic surface.

Fig. 5. (a) Oil- and water-absorption performance of SCF; (b) superhydrophobic/oleophilic surface of SCF-ODA. (oil: dimethyl silicone stained by Oil Red O)

Subsequently, the separation experiment for oil/water mixture was carried out and exhibited in Fig. 6. Several milliliter dimethyl silicone were poured into the water to form a floated oil layer. Afterwards, SCF-ODA was brought into the oil/water solution and a complete oil absorption occurred within 4 seconds (shown in Fig 6a), demonstrating a high-efficiency oil/water separation capability.

Fig. 6. (a) Digital photos showing the oil/water separation process by using SCF-ODA. (Red oil: dimethyl silicone stained by Oil Red O); (b) Dynamic

underwater absorption behavior of SCF-ODA. (Oil phase: dibromoethane stained by Oil Red O).

Besides, the SCF-ODA can also be used to achieve quick underwater absorption. As shown in Fig. 6b, a drop of dibromoethane (mass density = 2.17 g/cm^3) stained with Oil Red O sat at the bottom of the water. When SCF-ODA was immersed into the water and held by a pair of tweezers, the surface of the SCF-ODA appeared an obvious mirror reflection, deriving from the interface formed between the water and the entrapped air on the rough surface of SCF-ODA. Meanwhile, the dibromoethane can be absorbed completely in 3 seconds and the solution became completely clear. All these phenomena indicated that the modified SCF exhibited excellent oil/water separation behavior and removal of oil spillage and chemical leakage.

3.5. Super-absorption capacity of SiC-ODA towards high-viscosity oil and organic solvents

For the practical application of oil/water separation materials, their capacity towards high-viscosity oil is usually viewed as one of the most crucial issues. This is explained by the fact that almost half of the oil reserve cases are about high-viscosity oil. As reported in many pervious absorption works, the viscosity of model oils was usually below 500 mPa s [39-41], while for those oils with their viscosity range from 10^3 to 10^5 mPa s were hardly used.

As demonstrated in Fig. 7(a-d), two kinds of dimethyl silicone with their viscosity of 500 mPa s (MS-500) and 5000 mPa s (MS-5000) were applied as the

model crude oil in the absorption test. Fig. 7a and 7b indicated a droplet of MS-500 can be completely absorbed into the SCF-ODA within only 4 seconds (Movie S1). By comparison, when 200 μL MS-5000 were placed onto the surface of SCF-ODA (Fig. 7c and 7d), it took 22 seconds to achieve a complete absorption (Movie S2).

To improve the diffusion behavior of viscous crude oil and accelerate the oil absorption rate, Yu's team designed a Joule-heated graphene wrapped sponge (GWS). The hydrophobic graphene endowed the GWS with high oil/water separation efficiency while the Joule heat produced by the extra current would lead to a rapidly decreased oil viscosity. The oil absorption rate of the heated GWS increased by about an order of magnitude when compared with the unheated GWS. The results proved that compared with the unheated GWS, the oil absorption time of GWS decreased by 94.6%. When compared with Yu *et al.*'s report (8 μL within 6 seconds at 90 $^{\circ}\text{C}$), the SCF-ODA designed in the current work possessed a comparable oil-absorption rate. It must be particularly pointed that the oil absorption of SCF-ODA for high-viscosity oils was realized without any extra Joule heating, making it a superior absorption material for power-free oil-spill remediation.

Fig. 7. Absorption behaviour test: a drop of methylsilicone oil with the viscosity of 500 mPa s before (a) and after (b) absorption; a drop of methylsilicone oil with the viscosity of 5000 mPa s before (c) and after (d) absorption.

The oil absorption rate of different adsorbents in literature were summarized in Table 2. [42-46]. The superhydrophobic SCFs prepared in this study exhibited superior absorption efficiency towards high viscosity oils as compared to some other reported adsorbents.

Table 2. Absorption rate of different sorbents for viscous oils.

Temperature (°C)	Oil absorption (μL)	Absorption time (s)	Oil viscosity (mpa s)	Ref.
25	8	0.5	3	[42]
25	6	8.64	69.89	[43]
25	2040	180	86.5	[44]
90	8	6	100	[45]
20	4170	600	172	[46]
25	220	6	500	This study

In a typical process for the absorption of liquid droplets, as shown in Fig. 8, two steps including surface wetting and internal capillary imbibition have a strong effect on the absorption rate. While in the current study, oil absorption is a wetting-controlled process, because we found the oil droplet pass through the surface holes very soon after it dropped onto the SCF (Movie S1 and S2). For the surface wetting of liquid droplet, capillary, gravitational and viscous should be taken into account according the following equation (equation 2) [47]:

$$r(t) = \left[\left(\gamma_{LG} \frac{96\lambda V^4}{\pi^2 \eta} (t + t_0) \right)^{\frac{1}{2}} + \left(\frac{\lambda(t+t_0)}{\eta} \right)^{\frac{2}{3}} \frac{24\rho g V^{\frac{3}{8}}}{7.96^{\frac{1}{3}} \pi^{\frac{4}{3}} \gamma_{LG}^{\frac{1}{3}}} \right]^{\frac{1}{6}} \quad (2)$$

where γ_{LG} is surface tension of the fluid, V is drop volume, η is the viscosity of the fluid, ρ is density of the fluid, g is gravitational constant, λ is shape factor and t_0 is experimental delay time. According to the equation, the wetting time could increase with the increasing of viscosity.

Fig. 8. A proposed “two-step” mechanism for the oil absorption in SCFs

The subsequent capillary absorption is strongly related to the wetting behaviour on the hole walls that below the SCF surface. As so far, many models have been built

to investigate the liquid motion in the porous media [48-51]. According to the Benavente *et al.*'s investigation on the capillary imbibition occurred in the porous materials, the weight of liquid absorption $w_{(t)}$ as a function of time can be given by (equation 3) [52]:

$$\frac{W_{(t)}}{t^{\frac{1}{2}}} = CA \quad (3)$$

Where A is the cross-section area; C is determined by $\varphi\sqrt{r_{eff}\delta\sigma\tau\cos\theta}/2\mu$; where σ is the surface tension, θ is the contact angle, φ is porosity, τ is tortuosity, r_{eff} is the effective pore radius, δ is the pore shape factor and μ is the viscosity of the fluid. According to the above formula, the volume uptake per unit area has an inversely proportional relationship with the liquid viscosity and contact angle, implying that the enhanced oleophilicity caused by the decoration of low-surface-energy molecules (ODA) is beneficial for the rapid absorption in SCFs. Compared with energy promoted oil/water separation in Yu's work, two reasons are contribute to the enhanced oil absorption performance of modified SCFs: 1) a more hydrophobic hydrophilic surface. For the SCF-ODA, the grafting of long-chain alkane ODA was demonstrated to produce a superhydrophobic surface while graphene coated MF cannot achieve. 2) a more suitable porous structure formed in SCFs. Fig.S2 shows the morphology changes of SCF before and after sintering. We observed that the average pore size of sintered SCF was about 135 μm , which was significantly larger than SCF without sintering treatment (81 μm). This is due to the internally collapsing during the sintering, which will shorten the absorption path (in Fig S3) and improve the oil storage.

To further evaluate the absorption capacity of SiC-ODA quantitatively, the weight gain ratio was represented by the weight of the organic solvent absorbed by per unit weight of the dry SiC-ODA. (Fig. 9). A series of organic solvents were used for the absorption capacity of the SiC-ODA, including DMF, n-hexane, xylene, methyl silicone oil, dibromoethane, acetone, isopropyl alcohol, and methanol. The SiC-ODA was firstly immersed into the organic solvent for 1 minute and then weighed immediately to avoid solvent evaporation. The calculated data for the absorption capacities were compiled in Fig. 9. These solvents with different surface tension were common pollutants from our daily life or industries. Given that the bulk density of SiC is much higher than those materials made from cotton, polymer and carbon materials, the weight gain of SiC-ODA is obviously lower. Despite this, all the absorption capacities of SiC-ODA toward all the listed solvents were higher than 100%, because the porosity of SiC foam is as high as 84%.

Fig. 9. Absorption efficiency of the SCF-ODA for various organic liquids. Weight

gain here is defined as the weight ratio of the absorbate to the dried SCF-ODA.

4. Conclusion

In summary, by using VHPCS as the binder for SiC powders, a template-based strategy for the fabrication of SCFs was developed. The mechanical properties of SCFs have been optimized via adjusting the mass ratio between VHPCS and SiC powder and a maximum compression strength of 1.25 MPa was achieved. With a bio-inspired method, chemical-inert SCFs were activated and modified with ODA molecules. The obtained superhydrophobic/oleophilic SCFs demonstrated a high-efficiency and power-free way for high-viscosity oil absorption. It took only 22 seconds for the complete absorption of 200 μ L viscous oil with a viscosity of 5000 mPa s. The mechanism for the power-free and rapid absorption of viscous oil was proposed. The improved surface wetting and distinct porous structure were regarded as the critical factors.

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Movie S1: The absorption performance of SCF-ODA towards 200 μL methylsilicone oil with a viscosity of 500 mPa s. Movie captions : Two hundred microliter methylsilicone oil with a viscosity of 500 mPa s can be fully absorbed by SCF-ODA within only 4 seconds.

Movie S2 : The absorption performance of SCF-ODA towards 200 μL methylsilicone oil with a viscosity of 5000 mPa s. Movie captions : A complete absorption of 200 μL methylsilicone oil with a viscosity of 5000 mPa s can be realized within 22 seconds.

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