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ARTICLE TYPE

Low Cost and Robust Soot Dipped Polyurethane Sponge for Highly Efficient and Recyclable Oils and Organic Solvents Cleanup

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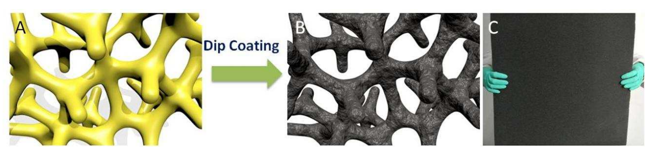
In this study, a very hydrophobic and superoleophilic sponge was fabricated by a homogeneous coating of soot on the polyurethane sponge (PUS) framework. The soot dipped polyurethane sponge (SPUS) exhibits very high efficiency and capacity for the selective absorption of oil and organic solvents from water. It has a largest absorption capacity that up to 45 times for pump oil and 86 times for chloroform with its original weight, along with high recyclability of more than 60 cycles. All the results indicate that SPUS has high potential for the practical application.

There has been rapidly growing worldwide concern about the urgent need to control releases of oil and other organic liquids during transportation and storage.[1] The adverse impacts on ecosystems and the long-term effects of environmental pollution caused by oil or other organic liquids have excited more public concern.[2] To address these environmental issues caused by oil spills, many approaches have been employed to clean up the oil, such as oil-sorption materials,[3] in situ burning, mechanical recovery, physical diffusion, enhanced bioremediation, oil skimmers, and superhydrophobic materials.[4] Among the above-mentioned methods, oil-water separating materials[5] with both superhydrophobic and superoleophilic properties have attracted a great deal of attention both in fundamental research and potential application in the field of oil-water separation. [6]

Recently, various superhydrophobic and superoleophilic materials such as, carbon nanotubes,[7] mesh films,[8] filter paper,[9] graphene[10] zeolites,[11] organoclays,[12] straw,[13] wool fibers,[14] polypropylene fiber, and alkyl acrylate copolymers have been attracting considerable interest in the field of oil-water separation. However, complicated preparation and difficult fabrication process of these materials limited their practical applications.[15] Soot is a daily waste which is very common in the countryside of China. It is easy to collect and has a large storage, which is from the burning of charcoal plant. Polyurethane is a kind of commercially available 3D porous material.[16] Owing to the high absorption ability, low density, and good elasticity, PUS has been provided as substrate for fabrication of oil absorbents.[17] However, due to the hydrophilic surface, it is impractical to be used as a selective and efficient oil absorbents in water. Therefore, it is necessary to modify it from hydrophilic to hydrophobic for removing oils from water. In view of this consideration, the soot networks may be used to increase the surface hydrophobicity by employing the high hydrophobic property and the nanoscale network for that the intrinsic hydrophobicity can be enhanced by surface roughness.[17,18]

In this communication, we report a facile and low-costs strategy to prepare very hydrophobic and superoleophilic materials through dip-coating process (Scheme 1). PUS was used as a frame for soot coating. Soot was selected to incorporate with sponges, resulting a very hydrophobic and superoleophilic substrate. Soot was controllably anchored on the sponge skeletons to regulate the sponge's characteristic to very hydrophobic (Water CA of 142.3 ± 1.2°). The as-fabricated soot based PUS absorbs a broad variety of oils and organic solvents with high selectivity, good recyclability, and excellent absorption capacities, approaching to 86 times of its own weight. The findings show promising development of advanced liquid-liquid separation or water treatment technology with environmental friendliness and lowest cost.



Scheme 1 Schematic of the PUS (A) with three-dimensional (3D) open structure and the SPUS (B) with conformal soot coating. (c) Photo of Large scale prepared SPUS

Fig.1 A and B show the TEM of the soot that hold a hollow structure. The SPUS sponges were prepared through a dip-coating (Fig. S1) and evaporation methods, which can be easily further developed to large scale (Scheme 1). The phase structure and purity of the soot was characterized by X-ray diffraction (XRD) in Fig. 1E. The reflectionspeaks (2θ) of the soot at28.6°, 40.7°, 50.3°, 58.8° and 66.7° are ascribed to the(110), (200), (211), (220) and (013) planes of carbon, which are similar to those of pure carbon (JCPDS No. 72-2091). These results suggest that soot are not amorphous carbon. Soot was further characterized by X-ray photoelectron spectroscopy (XPS) to investigate the surface nature of the carbon. The main peak at 283.3 eV is due to C 1S of carbon atoms and 531.3 eV is due to O 1S of oxygenate atoms (Fig. S3). The C1s band obtained from soot (Fig.1F) can be fitted into just one component which belong to C-C (Fig. S4). To prepare the super hydrophobic sponge, the commercially available PUS (Scaffold shown in Fig. S5) was dipped into an aceton dispersion of soot. After evaporation of the aceton in an oven at 80 °C for 3 hours, the soot was strongly attached to the skeleton of the PUS due to the van der Waals interactions.[7c,7d] Fig 1C and D show the SEM images of SPUS which demonstrates a three dimensional hierarchical porous structure.

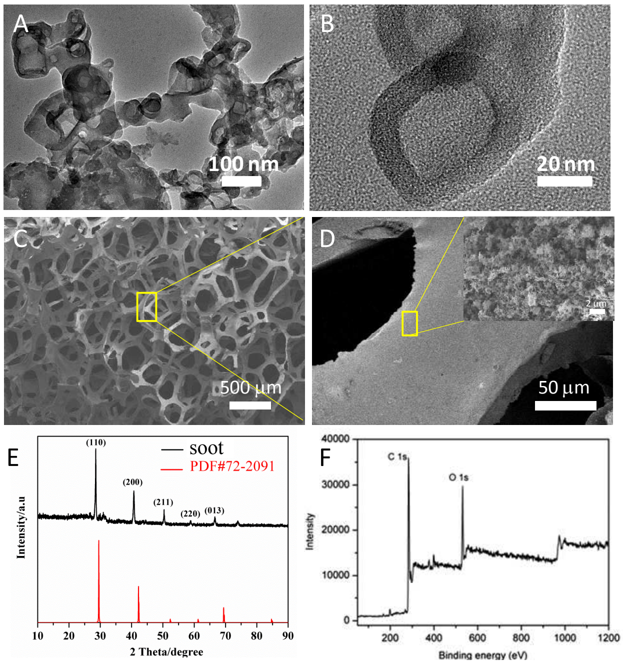


Fig.1 (A) TEM of the soot. (B) HRTEM of the soot structure. (C) and (D) Scanning electron microscope (SEM) image of the SPUS, showing the macroscale porous structure and the soot surface. The inset of (D) is a high-magnification SEM image showing the SPUS after soots coating. (E) XRD patterns and (E) XPS spectra of the soot.

As shown in Fig. 1D, the skeleton of PUS was fully coated by soot and formed a nanoscale porous surface with a dense coverage of soot. This nanoscale porous surface and hierarchical structure can be contributed to the hydrophobicity of the SPUS and thus provide high efficiency in absorbing oils and organic solvents. [19] We had test the surface areas and pore sizes of these materials through nitrogen sorption method and found that the surface areas of the soot, PUS and SPUS are 6.36, 0.69 and 9.14 m^2/g (Fig. S6). The pore sizes of soot are larger than 7 nm and have a wide size distribution from 7 nm to 60 nm (Fig. S7A). For SPUS, a pore size distribution from 10 nm to 100 nm was found (Fig. S7 B), which confirmed that the soot are strongly anchored on the PUS to form SPUS structure .

The wettability of as-prepared nanoscale sorbent is carried out as shown in Fig. 2A. A water droplet about 2 mL allowed contacting the surface of the SPUS, and the water contact angle (WCA) was 142.3 ± 1.2°, indicating that the SPUS is superhydrophobic. In contrast, when 2 mL pump oil droplet is dropped on its surface, the pump oil droplet immediately spread on the SPUS with oil contact angle (OCA) of 0°, which indicates that the sample is superoleophilic. Such superior hydrophobicity of the 3D hybrid SPUS is due to the nano-roughness (Fig. 1A) created by the SPUS forest on the PUS surface and the air interfaces in the macroscopic voids of the 3D structure of the PUS skeleton. The SPUS can be floated on water surface since their density is only 1% of water. In comparison, conventional cleaning PUS is hydrophilic and sank below the surface level when immersed in water (Fig. 2B). The 3D porous structure and surface hydrophobicity of the SPUS make it an ideal candidate for the removal of pollutants such as oils and organic solvents from water. Fig. 2C-H shows the strong pump oil sorption of SPUS. When the SPUS was brought into contact with an oil layer (stained with Sudan red 5B) on water surface, the oil was completely absorbed within 40 s. The SPUS could float on the water surface after sorption of the oil, indicating its potential for the facile removal of oil spillage and chemical leakage.

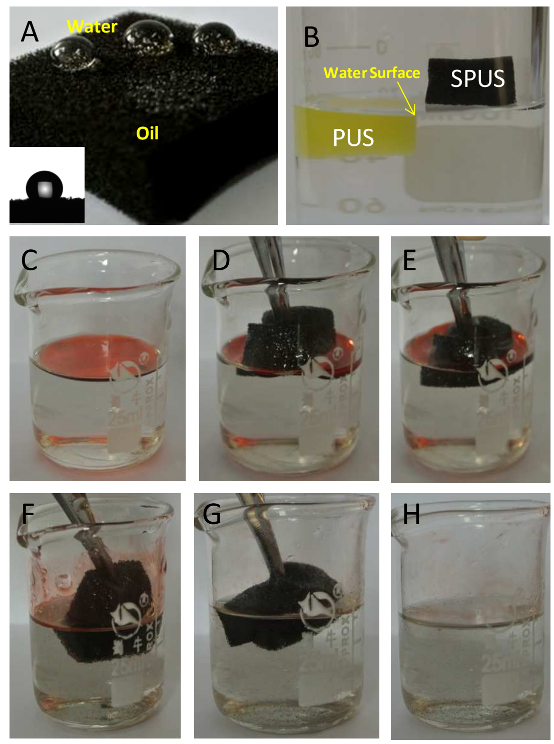


Fig.2 (A) Photograph of water and oil droplets on the surface of SPUS. (B) When a piece of the PUS treated sponge were placed in a water bath, the PUS absorbed water and sank to below the surface level while the SPUS was floating on the water surface. (C)-(H) Photographs demonstrating the removal of an oil droplet from water using SPUS.

The different diameters and porous morphology of SPUS also show tiny influence to the wettability of as-prepared samples. Fig. 3A (Blacak cubic point) shows the dependence of the contact angle with soot loading. With the increasing of content of soot, the WCA of SPUS increased slightly. That is, the soot modified PUS with high surface roughness could be the main reason for its very hydrophobicity and superoleophilicity. As shown in Fig. 3A (red point), the absorption capacity of the SPUS for the pump oil increases with the soot loading. At the soot loading of ~20 wt% (SPUS density: 0.03 g/cm^3), the absorption capacity reaches the highest value of ~56 times the SPUS weight, which is better than the absorption capacity of PUS. The relation between the soot loading and contact angle is listed in Table S1. At the loading of 9 wt%, the contact angle reaches the highest value of 133.3°, indicating a high hydrophobicity for the SPUS. When the soot loading is higher than ~20 wt%, change of contact angles was observed from 135.6% to 142.4%. These results indicate that the increased absorption capacity is ascribed to the hydrophobicity enhancement by increased soot loading. To explore the scope of contaminants that can be absorbed by SPUS, pump oil is tested and the results are shown in Fig. 3B. It only took 50 s for the SPUS to reach its maximum absorption capacity which means that the SPUS could be high efficiency oil absorbent.

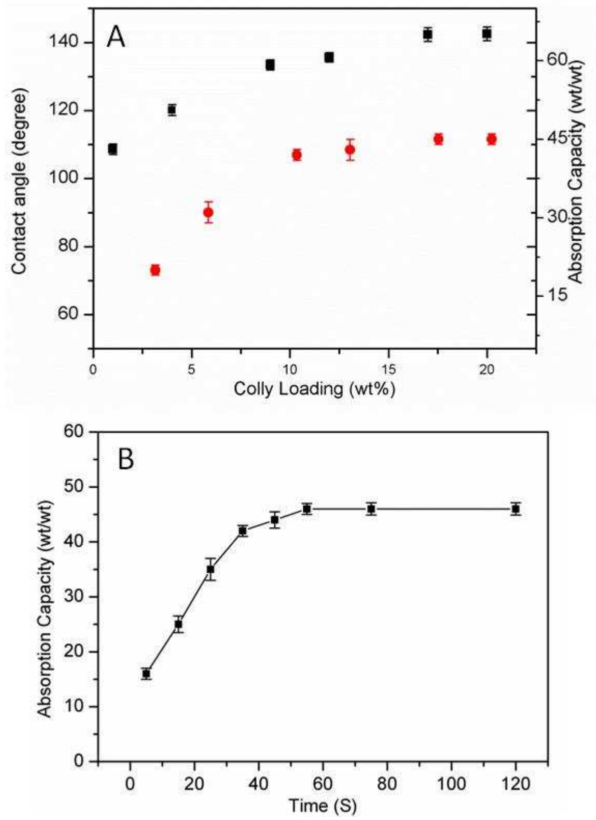


Fig.3 (A) Dependence of the contact angle (Black Cubic Point) and absorption capacity (Rea point) on the soot loadings of SPUS. (B) Dependence of the time for absorption capacity of SPUS.

In addition, the SPUS can be used to for the rapid absorption of organic solvents whose densities are higher than water by physically pressing it below the surface. To explore the loading of contaminants, we define the weight gain (wt%) as the weight of absorbed substance per unit weight of the dried SPUS. Various types of organic liquids were studied, such as the commercial petroleum products (e.g. pump oil), fats (e.g. soybean oil, olive oil) and organic solvents, such a dichloromethane, dichloroethane, ethylacetate and hexane. The SPUS showed a very high sorption capacity for all of the aforementioned organic liquids. The absorption capacities of SPUS for various oils and several organic liquids are shown in Fig.4A. The oil-absorption capacity, Q, of the sponge was calculated as $Q = (M_2 - M_1)/M_1$ according to previous reports,[20] where M_1 and M_2 represent the weights of the sponge before and after oil absorption, respectively. The data in Fig. 4A shows that the Q values of the SPUS can reach a maximum of 86 g g^{-1} for chloroform. This is an extraordinary high value. The adsorption capacity depends not only on the density but also on the viscosity and surface tension.[18,21] For example, chloroform has a higher density than hexane (1.48 vs. 0.66 g cm^{-3}), the adsorption capacity of chloroform is higher. This can be explained by the higher viscosity (0.56 vs. 0.33 cSt) and surface tension (0.027 vs. 0.018 g/N m^{-1}) of chloroform than that of hexane. As expected, for each of the organic liquids, the Q value of the PUS was lower than that of the SPUS, even though the values are still higher than those for most of the other absorbents shown in Table S1. There are probably two reasons for the differences in Q values. Firstly, the hollow structure of the soot (Fig. 1C) makes the SPUS more efficient than that of the PUS. Secondly, the SPUS has fewer polar functional groups and it is oleophilic, so it has a stronger affinity for organic liquid, which results in a higher absorption capacity.[22]

Despite the relatively lower absorption capacity than that of graphene sponge[23] and graphene-CNT hybrid foam,[24] the procedures to produce SPUS are simple, cost effective, and scalable. In the application of contaminant removal, both large absorption capacity and high recyclability are required. The reusability of the SPUS was checked. In the recycling experiments, the absorbed pump oil was extracted from the SPUS by using petroleum ether rinse. The absorbed organic solvents (Chloroform, dichromethane and ethyl acetate) were removed by directly heating the SPUS at 80 °C in an oven. As shown in Fig. 4B, the absorption capacity of the SPUS does not show obvious degradation even after 60 cycles, suggesting a highly stable absorption performance. Comparing with the maximum sorption capacity reported,[25,18] the sorption capacities during reuse were stable and close to the maximum sorption capacities, which means that the PUS networks were still in excellent condition after 60 cycles.

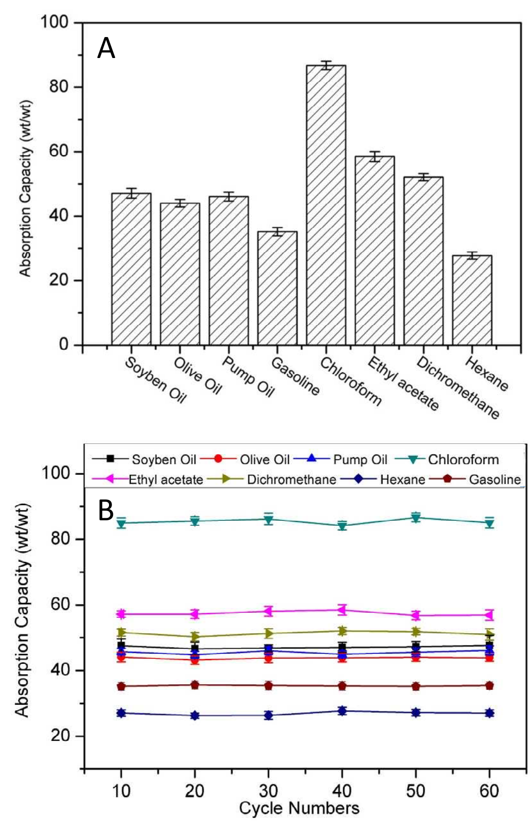


Fig.4 (A) Absorption capacity of the SPUS for various oils and organic solvents. (B) Absorption recyclability of the SPUS.

Conclusions

In summary, we have presented a dip-coating method to prepare a novel hybrid soot polyurethane sponge. The porous structure of the PUS served as the 3D scaffold to anchor the soot forest. The SPUS exhibits hydrophobic properties owing to its bulk porous structure and nano-roughness surface and the hydrophobicity. The absorption capacity investigation demonstrated that the SPUS is efficient and stable in absorbing a wide range of oils and organic solvents. Due to the much more lower cost than other absorption materials, SPUS is considered to be a very promising absorbent for the treatment of oil spills or oil water separation.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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