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Carbon Aerogel from Winter Melon for Highly Efficient and Recyclable Oils and Organic Solvents Absorption

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Supporting Information

ABSTRACT: Direct conversion of biomass to carbon aerogel provides a promising approach to developing absorbent materials for spilled oils and organic solvents recovery. In this work, three-dimensional carbon aerogels were fabricated via a hydrothermal and post-pyrolysis process using winter melon as the only raw materials. The winter melon carbon aerogel (WCA) prepared shows a low density of 0.048 g/cm^3, excellent hydrophobicity with a water contact angle of 135°, and selective absorption for organic solvents and oils. The absorption capacity of WCA for organic solvents and oils can be 16−50 times its own weight. Moreover, distillation can be employed to recover WCA and harvest the pollutants. Over five absorption−harvesting cycles, the absorption capacity of WCA to organic solvents and low boiling point oils can recover almost 100% of its starting capacity. With a combination of low-cost biomass as raw materials, green preparation process, low density, and excellent hydrophobicity, WCA as an absorber has great potential in application of spilled oil recovery and environmental protection.

KEYWORDS: *Biomass, Carbon aerogel, Water−oil separation, Absorption, Recyclable*

■ INTRODUCTION

Two-thirds of Earth is covered by water. Water pollution as a result of oil spills, toxic chemical leaks, and industrial wastewater discharge has led to severe environmental and ecological problems.[1,2] For example, on April 20, 2010, a gas release and subsequent explosion occurred on the *Deepwater Horizon* oil rig in the Gulf of Mexico. The total crude oil discharge has been estimated at 4.9 million barrels. Due to the months-long spill, along with adverse effects from the response and cleanup activities, extensive damage to marine and wildlife habitats, fishing and tourism industries, and human health problems have continued through 2014.[3,4] Although many conventional methods such as combustion, oil boom or oil skimmer, physical diffusion (aided by dispersants), and biodegradation have been used for oil recovery, they either show poor efficiency or may introduce other types of containments during the cleanup procedure.[4−6]

Recently, much attention has been paid to developing porous materials as oil absorbers because they can achieve oil−water separation via a simple, fast, and effective absorption process.[4−19] Generally, an ideal absorbent material should have high oil absorption capacity, high selectivity, low density, and excellent recyclability, and it should be environmentally friendly. Thus, various natural absorbers such as expanded perlite and zeolites, organic materials such as wool fiber, activated carbon, and sawdust have been used because of their microporosity.[15−19] However, these conventional materials show low absorption capacity and nonselective absorption to both water and oil. To overcome these limitations, particular attention has been paid in recent years to the development of carbon-based aerogels, such as carbon fiber aerogel, carbon microbelt aerogel, carbon nanotube (CNT) aerogel, and graphene aerogel, which have three-dimensional (3D) structures and outstanding properties, such as low density, high porosity, large specific surface area, and surface hydrophobicity. Those properties have proven to be advantageous by increasing absorption capacity and facilitating selective absorption of oil or hydrophobic organic solvents from water.[4−14] For example, aerogels made from twisted carbon fibers can absorb a wide range of organic solvents and oils with a maximum sorption capacity up to 192 times the weight of the pristine aerogel.[5] Graphene aerogel with ultralow density can absorb oils and organic solvents 20−86 times its own weight.[11] The CNT sponge with a porosity of higher than 99% can absorb a wide range of solvents and oils with excellent selectivity and absorption capacities up to 180 times its own weight.[12] However, the harmful and expensive precursors, complicated process, and complex equipment involved in CNT and graphene aerogel fabrications dramatically hamper their large-scale production for industry applications, which pushes us to explore a facile, economic, and

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environmentally friendly strategy for massive production of new carbon-based aerogels.[4−13]

To date, there is a trend to produce carbon-based materials from biomass, as it is cheap, easy to obtain, sustainable, and environmentally friendly.[5,8,20] Generally, biomass can be directly transformed into carbonous materials by a well-established hydrothermal carbonization (HTC) process under mild heating conditions.[20−24] The winter melon (wax gourd) is a fast growing and long season vegetable consumed widely in Asia and other semi-tropical countries.[25,26] This vegetable contains more than 90% water and less than 10% polysaccharide, making it a promising raw material for fabrication of highly porous structure materials. In this work, 3D carbon aerogels were made by a HTC and post-pyrolysis process using winter melon as the raw material. The winter melon carbon aerogel (WCA) prepared has low density and high hydrophobicity, which ensure its broad absorption spectrum for organic solvents and various oils. The absorption capacity of WCA is 16−50 times its weight, comparable to other carbon-based aerogels. Considering the high performance, cheap raw materials, and green synthetic method, WCA is believed to have great potential for removing petroleum products and toxic organic solvents.

EXPERIMENTAL SECTION

Materials. Fresh winter melon (wax gourd), sunflower oil, corn oil, and sesame oil were obtained from local markets. Methanol, ethanol, 2-propanol, ethylene glycol, acetone, chloroform, hexane, cyclohexane, toluene, dimethylformamide (DMF), butyl stearate, crude oil, and Sudan red were purchased from Sigma-Aldrich Co., Ltd. Gasoline and diesel were purchased from Abu Dhabi National Oil Company. Vacuum pump oil was purchased from Rocker Scientific Co., Ltd.

Preparation of Carbon Aerogels. First, the rind, soft pulp, and seeds from winter melon were removed. Then the flesh of the winter melon was cut into an appropriate shape and volume (around 20 cm^3) and placed into a Teflon-lined stainless steel autoclave. The autoclave was heated at 180 °C for 10 h under self-generated pressure in a closed system. The winter melon hydrogels were immersed in hot water (around 60 °C) for 2 days to remove soluble impurities. The remaining winter melon aerogels (WA) were obtained by freeze-drying. Finally, to fully convert WA to WCA and improve the hydrophobicity, the WAs were placed in a tube furnace and pyrolyzed at 800 °C for 1 h in N_2 atmosphere.

Characterization. The morphology of WA and WCA was imaged by a FEI Quanta FEG 250 scanning electron microscopy (SEM). All optical pictures used in this paper were taken by a Canon digital camera (IXUS 70). The water contact angle of WCA was measured on a Kyowa contact angle system (DM501) at room temperature. The porosity of WCA (P_{WCA}) was calculated through the following equation

$$P_w = (1 - \rho_w/\rho_c) \times 100\%$$

ρ_w and ρ_c are the density of WCA and amorphous carbon, respectively, and the value of ρ_c is 2 g/cm^3 (typical value for carbon black or activate carbon).[27]

Absorption of Oils and Organic Solvents. In a typical test, a piece of WCA (with volume around 1 cm^3) was placed in contact with the organic solvents or oils for 10 s, and then, it was taken out for mass measurement. The mass of a piece of WCA aerogel before and after absorption was recorded for calculating the mass gain. The absorption capacity of WCA was calculated by the ratio between the maximum absorbed oil quantity, m_{oil}, and the WCA's own mass, m_{wca}. The volume-based absorption capacity was given by $V_{\mathrm{oil}}/V_{\mathrm{wca}} = (m_{\mathrm{oil}}\rho_{\mathrm{wca}})/(m_{\mathrm{wca}}\rho_{\mathrm{oil}})$, where ρ_{wca} and ρ_{oil} are the density of WCA and the oils, respectively.[9]

RESULTS AND DISCUSSION

The sponge-like winter melon hydrogel (WH) was prepared by a simple HTC process directly from the flesh of the winter melon. After the HTC treatment, as shown in Figure 1a and b, the color of the starting winter melon turned from white to black due to the carbonization of the biomass. Then, the water from the WH was removed by freeze-drying to obtain winter melon aerogel (WA). The representative SEM image of WA is presented in Figure 2a, which shows an interconnected 3D porous structure with pore size in the range of several hundred micrometers. Although the density of WA obtained is low, it floats beneath the water surface owing to its hydrophilicity and high absorption ability toward water. In addition, WA shows a dark brown color (Figure 1c), indicating that low temperature HTC treatment cannot fully convert the tissue of winter melon to carbon. Further pyrolysis treatment of WA at 800 °C under a N_2 atmosphere leads to the evaporation of volatile organic species and to the formation of WCA (Figure 1d). After pyrolysis, the volume of WCA is only 23% of that of WA, which shows a low density of 0.048 g/cm^3. Compared with WA, WCA shows a similar 3D structure with a pore size around 200 μm (Figure 2b). Furthermore, WCA possesses an ultrahigh porosity of more than 97.5%, which is only slightly lower than those of CNT aerogels (99.5−99%) and graphene aerogels (99.5−98%).[8,12,28−31]

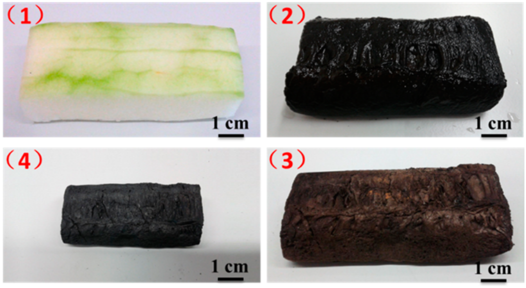
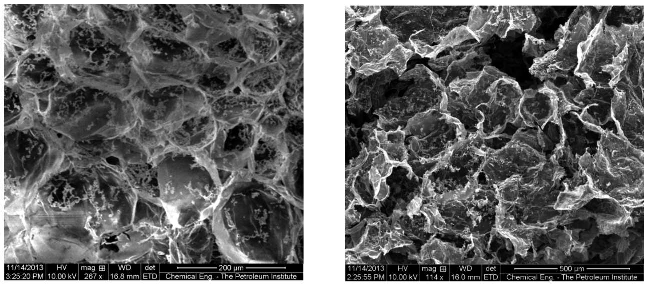


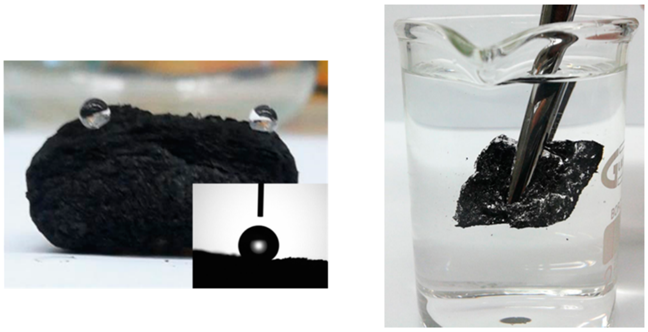
Figure 1. Optical images of raw winter melon (a), winter melon hydrogel (b), winter melon aerogel (c), and winter melon carbon aerogel (d).



(a) (b)

Figure 2. SEM images of winter melon aerogel before (a) and after (b) pyrolysis.

The intrinsic hydrophobicity of an absorbent is critical to achieve water−oil separation. While WA can absorb water effectively due to its hydrophilicity, WCA is hydrophobic and can support a spherical water droplet on its surface (Figure 3a). The contact angle image of WCA is shown in the Figure 3a inset where a water droplet deposited on the WCA surface is almost perfectly spherical with a contact angle of about 135°,



(a) (b)

Figure 3. (a) Optical image of water droplets with spherical shapes on the surface of WCA, showing intrinsic hydrophobicity. Inset is the water contact angle image of WCA. (b) Air bubbles entrapped at the interface between the aerogel and the surrounding water.

demonstrating its intrinsic hydrophobicity. To further confirm the hydrophobicity of WCA, it was held by a pair of tweezers and pushed to be immersed into the water. As shown in Figure 3b, air bubbles entrapped at the interface between the aerogel and the surrounding water are clearly observed. After releasing the external force, WCA could float immediately on the water surface without the absorption of water. Interestingly, WCA also has low affinity to water. When water droplets were dropped at the corner part of a WCA, a flow of water bouncing off the surface can be clearly observed (Video S1, Supporting Information). By contrast, when organic solvents or oil droplets come into contact with the WCA surface, they spread quickly on the surface and permeated it thoroughly, showing WCA's excellent oleophilic property.

The 3D structure, low density, high porosity, and excellent hydrophobicity and oleophilicity of WCA make it an idea candidate for the absorption of spilled oils and organic solvents from water. In Figure 4a, a piece of WCA sample selectively and completely absorbs the artificial oil contaminant (stained with Sudan red) from the water surface. The absorption process proceeded rapidly upon even slight contact between WCA and the target oil. The WCA saturated with oil can float on the surface of the water due to its low density and hydrophobicity and is therefore easily removed.[5] Furthermore, WCA can absorb oil and high density solvents (e.g., chloroform) from the bottom of the water. In Figure 4b, when a piece of WCA is immersed into the water and put in contact with the chloroform droplet (stained with Sudan red), it absorbed the chloroform from the water completely and rapidly. No water in the saturated WCA can be found, which shows very high selective absorption for the organic solvents and oils. These results indicate that WCA has great potential for the facile removal of oil spillage and chemical leakage.

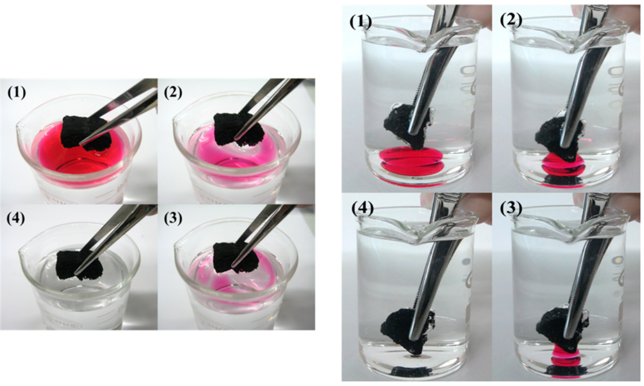


Figure 4. Removal of corn oil from the water surface (a) and chloroform from underwater (b) by a piece of WCA. Corn oil and chloroform were dyed with Sudan red to aid observation.

In order to study the absorption efficiency of WCA quantitatively, a series of organic liquids were investigated, including commercial oils (gasoline, diesel, pump oil, corn oil, sesame oil, sunflower oil, and butyl stearate) and crude oil, water-miscible solvents (methanol, ethanol, 2-propanol, ethylene glycol, acetone, and DMF), and water-immiscible solvents (hexane, cyclohexane, toluene, and chloroform). These materials are common pollutants in our daily lives as well as from industry. It is shown in Figure 5 that WCA has a high absorption capacity for all of the aforementioned liquids. The absorption capacity for gasoline, diesel, and crude oil is 24, 27, and 25, respectively. The absorption capacity of absorbent for various liquids is determined not only by the surface characteristics of the solid phase but also by the properties of liquids like density, surface tension, and hydrophobicity. Among all the organic liquids studied, chloroform shows the largest absorption capacity of 50. This is because chloroform has

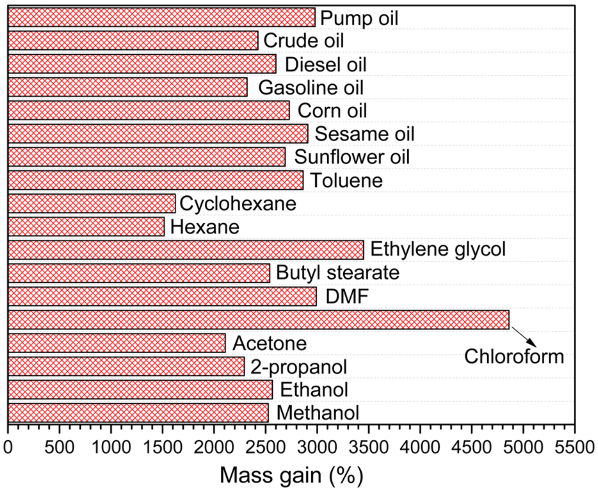


Figure 5. Absorption capacity of WCA for oils and organic solvents.

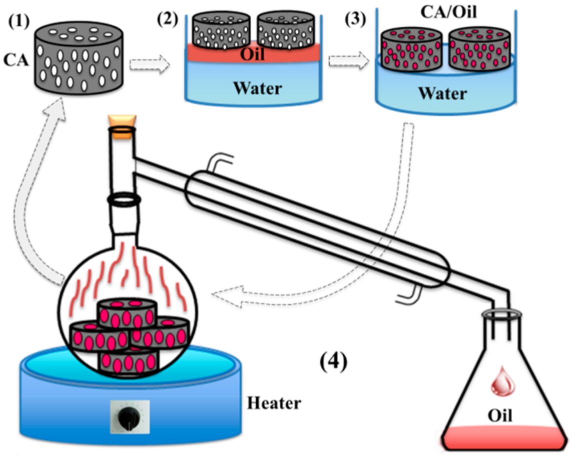
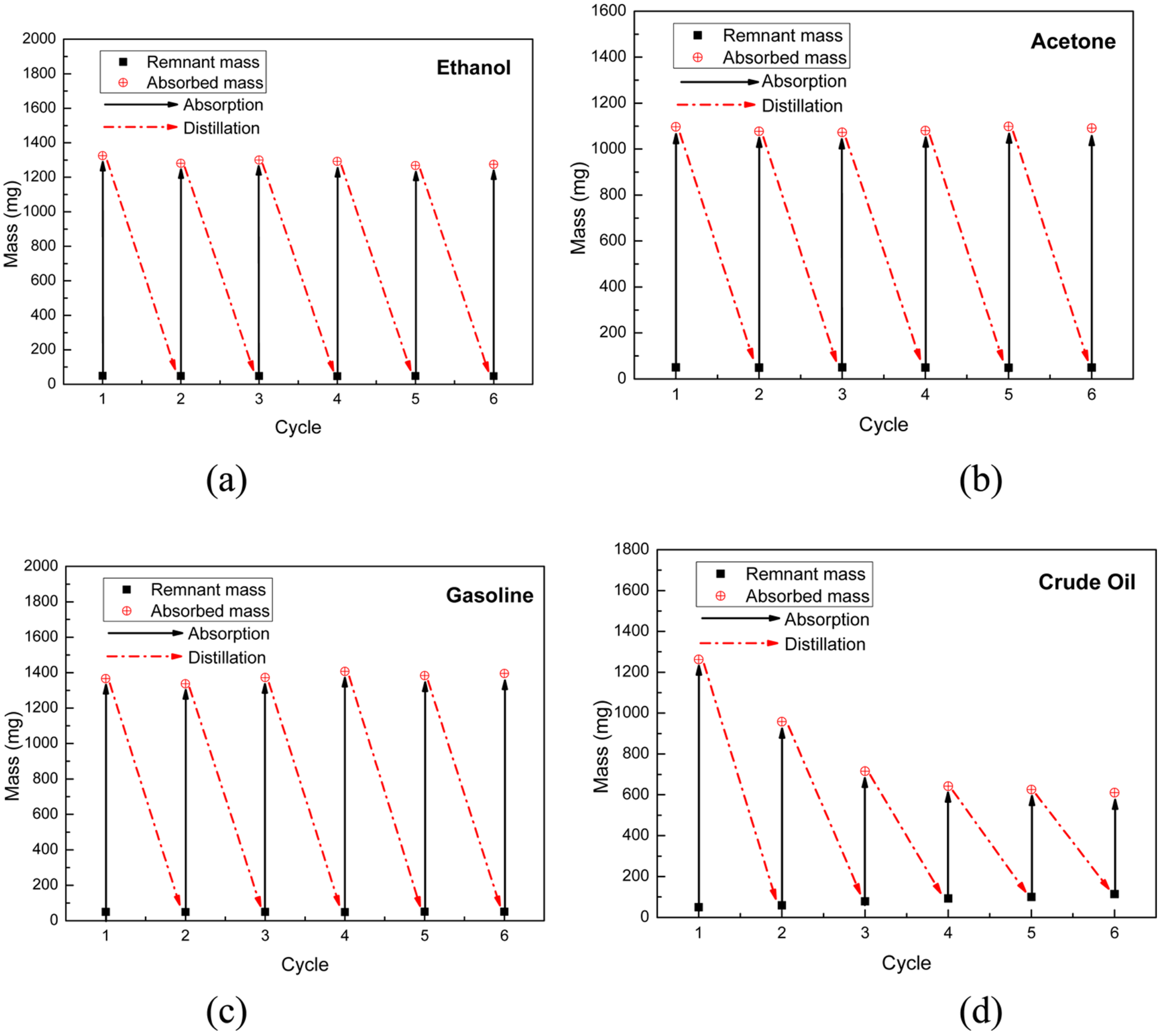


Figure 6. Schematic diagram of WCA recycling process: (1) original WCA, (2) absorption of oil on the surface of water, (3) WCA full of oil, and (4) regeneration of WCA and collection of oil with a distillation process.

Table 1. Comparison of Various Absorption Materials

absorption materials	absorption capacity (g/g)	cost of raw materials	sustainability of raw materials	fabrication process	refs
expanded perlite	3.2–7.5	low	no	easy	15
zeolite	5	low	no	complicate	16
wool-based nonwoven material	11–16	medium	yes	medium	17
sawdust	3.77–6.4	low	yes	medium	19
magnetic CNT sponge	49–56	high	no	complicate	6
CNT sponge	80–180	high	no	complicate	12
graphene sponges	54–165	medium	no	complicate	10
spongy graphene	20–86	high	no	complicate	11
carbon fiber aerogel	50–192	low	yes	easy	5
carbon microbelt aerogel	56–188	low	yes	complicate	14
WCA	16–50	low	yes	easy	present work



(a) (b) (c) (d)

Figure 7. Recyclability of WCA for absorption of ethanol (a), acetone (b), gasoline (c), and crude oil (d) with a distillation method.

the highest density, low surface tension, and high affinity to the hydrophobic surface of WCA.[2] In general, WCA can take up these oils and solvents at 16–50 times its own weight and shows high absorption capacity for liquids with higher density. The absorption capacities of WCA are much higher than those of conventional absorbers, such as expanded perlite and zeolite and activated carbon (Table 1).[14–18] Although the absorption capacity of WCA for the aforementioned liquids is not the highest ever reported, the volume absorption capacity of WCA is around 97%, which is comparable to those values (95–99.5%) obtained using carbon-based aerogel.[4−13] Compared to CNT aerogel and/or graphene aerogel, WCA has the advantage of low cost by using the green synthetic method. The reason for the high oils and organic solvents absorption capacity is that WCA has high porosity (>97.5%), and organic liquids can be stored in the interconnected pores inside. Capillaries are believed to be the force driving the oils and organic solvents into the aerogel. The capillary flow is further strengthened by the oleophilic surface when the oils spread into the inner pores of the aerogel, resulting in a high absorption capacity.[9]

The recyclability of absorbent and the removal efficiency of pollutants also play important roles in pollution control and environmental protection because most pollutants are either precious raw materials or toxic, e.g., crude oil and toluene.[5,11] As illustrated in Figure 6, distillation is employed to recover pristine WCA and harvest the pollutants, unlike the combustion process that will waste the precious raw materials. The recyclability test has been conducted between WCA, typical organic solvents (ethanol and acetone), and oils (gasoline and crude oil). After the liquids have been absorbed by WCA, the saturated WCA was heated to 100 °C to release the vapor of low boiling point liquid (ethanol, acetone, and gasoline) and 300 °C to release the vapor of crude oil. The recovered WCA and various liquids were collected for recycling.

The absorption and distillation process was repeated at least five times to investigate the recyclability of WCA. The recyclable absorption behavior of WCA to organic solvents and low boiling point oil (for instance, ethanol, acetone, and gasoline) is similar, and no obvious change in the absorption capacity of WCA was observed. As shown in Figure 7a−c, after five absorption−harvesting cycles, the absorption capacity of WCA can recover almost 100% because the size and structure of WCA stayed the same during the entire process. However, for oils of multi-composition, such as crude oil, the saturated absorption capacity goes down with usage. The absorption capacity of WCA to crude oil after one and five test cycles is 76% and 48% of its original absorption capacities, respectively. The decrease in absorption capacity is due to the residual solid phase inside the aerogel, such as the asphalt in crude oil, which cannot be removed by distillation.

CONCLUSION

In conclusion, WCA has been fabricated via a HTC post-pyrolysis process using winter melon as raw materials. This two-step process is a totally green, chemical-free, synthetic method with cheap and ubiquitous biomass as the only raw material. The WCA prepared showed a low density of 0.048 g/cm^3 and excellent hydrophobicity with a water contact angle of 135°. The absorption capacity of WCA can be 16−50 times its own weight for organic solvents and oils. Distillation was employed to regenerate of WCA and harvest the pollutants. After five absorption−harvesting cycles, the absorption capacity of WCA to organic solvents and low boiling point oils can recover to almost 100% of the starting value. The absorption capacity for crude oil decrease to 48% due to the solid residues. With a combination of low-cost biomass as raw materials, green preparation process, low density, and excellent hydrophobicity, WCA is highly promising as an economic, efficient, and safe absorbent for environmental and ocean protection.

ASSOCIATED CONTENT

Supporting Information

Video S1: The video shows that a flow of water bounces off of the surface of WCA. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

Y.L. conceived and designed the project. Y.L., Y.S., K.P., and S.A. fabricated the materials and carried the experiments. All authors contributed to the data and discussions regarding the research. Y.L. and K.L. wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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