

Highly Efficient and Recyclable Carbon Soot Sponge for Oil Cleanup

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Supporting Information

ABSTRACT: Carbon soot (CS) has the advantages of cost-effectiveness and production scalability over other carbons (i.e., graphene, CNTs) in their synthesis. However, little research has been conducted to explore the potential applications of CS. In this study, we demonstrated that a common daily waste—CS—can be used for developing a cost-effective absorbent (CS-sponge) to remove oil contaminants from water. The CS was synthesized by an ethylene-oxygen combustion flame. The CS-sponge was prepared via a dip-coating method. Without further surface modification and pretreatments, the CS-sponge demonstrates high absorption capacities (up to 80 times its own weight) for a broad spectrum of oils and organic solvents with a recyclability of more than 10 times. These research results show evidence that the CS-sponge is promising in environmental remediation for large-scale, low-cost removal of oils from water.

KEYWORDS: carbon soot sponge, hydrophobicity, water contact angle, oil absorption, environment protection



1. INTRODUCTION

Over the years, water pollution resulting from oil spillage and industrial organic pollutants has emerged as a critical issue on a global scale, imposing threats to the ecosystem, human health, and economic growth.^{1–5} To address this challenge, many efforts have been made to develop efficient absorbents, such as activated carbon,⁶ expanded graphite,⁷ microporous polymers,^{8–12} carbon-nanotube (CNT) sponge,¹³ Fe/CNT composites,^{14–16} and graphene sponge,³ for separating and removing the contaminants from water. Among these absorbents, carbon-based absorbents demonstrate superior efficiency in the removal of oils.^{2–4,7,16–23} However, the high production costs of these absorbents limit their wide adoption.^{2,5,6,21} For example, activated carbon needs surface modification for improved oil absorption efficiency due to its hydrophilic nature.⁶ Expanded graphite has to be wrapped in plastic bags, causing handling inconvenience and poor recyclability.^{2,7} Large-scale synthesis of CNT- and graphene-based sponge is hampered by preparation complexity and the lack of large-size templates.^{2,5,20} Therefore, it is important to develop new absorbents with high absorption capacity, recyclability, scalability, and low cost to address the global-scale environment challenges.

As a carbon family member, carbon soot (CS), which is generated from incomplete combustion of hydrocarbons (e.g., candles, diesel exhaust, combustion flame, exhausted fumes from power plants),^{24–28} has demonstrated the advantages of cost-effectiveness and production scalability over graphene, CNTs, and activated carbons in their synthesis.^{6,7,13} However,

up to now, CS has received little attention on exploring its potential applications, compared to the extensive study on graphene, CNTs, and activated carbons.^{24,29,30} In 2006, Uchida et al. reported the synthesis of CNTs using CS from diesel engine.²⁹ Recently, Xu et al. employed CS generated from candles for transparent robust superamphiphobic coating.²⁴ These works demonstrated that the common daily waste—CS—can be made useful and profitable, instead of threatening the environment and human health.^{31–34}

In this study, it is demonstrated that CS can be used for developing a cost-effective absorbent (CS-sponge) to remove oil contaminants from water. The CS-sponge has been developed by a simple dip-coating method.³ CS is abundant, is low cost, and can be easily obtained in most combustion processes. The CS used for preparing the CS-sponge was synthesized by an ethylene-oxygen combustion flame. A melamine sponge with a porous structure is commercially available at low cost. It was used in this study as a skeleton for hosting the CS. CS was introduced into the porous structure by dip coating in a 1,2-dichloroethane (DCE) solution. Without further surface treatment, the CS-sponge has a high absorption capability for a large range of applications, from oils to organic solvents. The CS-sponge has an absorption capacity of 25–80 times its own weight and can be recycled more than 10 times without obvious degradation in absorption capacity. Therefore,

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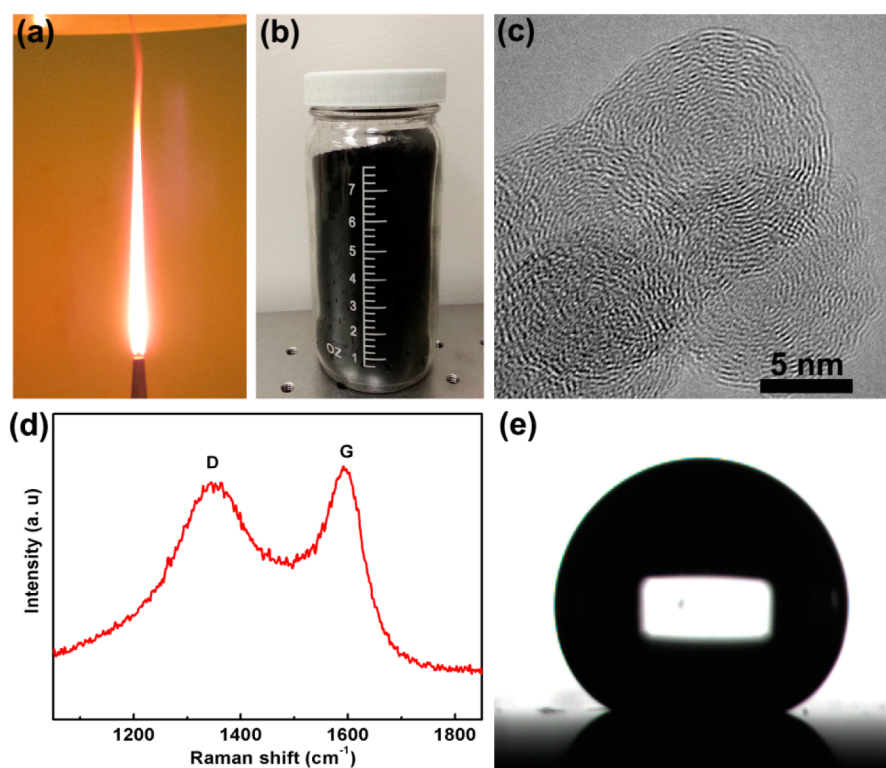


Figure 1. (a) Photograph of a combustion flame to synthesize CS, (b) as-grown CS (8 g) in a bottle, (c) TEM image, (d) Raman spectrum of CS, and (e) contact angle of a water droplet on a CS surface ($\sim 140^\circ$).

the CS-sponge provides a promising remedy for water pollution.

2. EXPERIMENTAL SECTION

2.1. Synthesis of CS. The growth of CS was performed using a combustion flame process in open air using ethylene (C_2H_4) and oxygen (O_2) as precursors with a flow ratio of 5:3. Figure 1a shows a welding torch with a 1.5 mm orifice tip for generating the flame. The CS was collected by placing a silicon wafer on top of the flame.

2.2. Preparation of CS-Sponge. The CS-sponge was prepared by dip-coating.³ First, 25 mg of as-grown CS was dispersed in 20 mL of DCE solution, followed by a 60 min sonication. Then, melamine sponge, which was cleaned by acetone and dried in an oven ($80^\circ C$), was immersed in the CS dispersion. The CS-coated sponge was again dried in the oven at $80^\circ C$ for 2 h. The CS loading on the sponge was defined as the weight ratio $(W_{CS-sponge} - W_{sponge})/W_{sponge} \times 100\%$, where $W_{CS-sponge}$ and W_{sponge} are the weight of the CS-sponge and original melamine sponge, respectively.

2.3. Absorption Measurement. In a typical absorption measurement, the CS-sponge was immersed into different oils and organic solvents until saturation. The absorption capacity (κ) was defined as the weight-gain ratio of the CS-sponge, which can be calculated using the following equation:⁶

$$\kappa = (W_{\text{saturated absorption}} - W_{\text{initial}})/W_{\text{initial}} \quad (1)$$

where W_{initial} and $W_{\text{saturated absorption}}$ are the weight of the CS-sponge before and after oil/solvent absorption, respectively.

2.4. Characterization. The as-grown CS was characterized by a field-emission transmission electron microscope (FEI, Tecnai G2 F30, 300 kV), a Renishaw inVia dispersive micro-Raman spectrometer with a 514 nm excitation source, and an FTIR spectrometer (Nicolet Avatar 380). The density of the CS was obtained by pressing the CS powder using a hydraulic screw press (model 341-20 from Loomis Engineering & MFG Company, Newark, NJ) at 850 MPa for 15 min. The morphology of the CS-sponge was characterized using a field-emission scanning electron microscope (Hitachi, S4700 FESEM system, with an

ultimate image resolution of 1.2 nm at 25 kV). Static water contact angle measurement was carried out using a contact angle goniometer (Powereach, JC2000D, China). The Brunauer–Emmett–Teller (BET) surface area and pore volume were measured by N_2 adsorption using an adsorption apparatus (Micromeritics, ASAP 2020, USA). A degassing process was used to remove the adsorbents on the sample. The degassing was in a vacuum with 0.3 mmHg for 30 min at $250^\circ C$. The pore size distributions were calculated by applying the density functional theory (DFT) to the N_2 isotherms using the microactive interactive data analysis software.

3. RESULTS AND DISCUSSION

The CS used to prepare the CS-sponges was synthesized by a combustion flame method. Figure 1a shows a photograph of a tabletop demonstration unit of an ethylene-oxygen combustion flame used for CS synthesis. The combustion method can be developed to an industrial scale. Figure 1b shows a bottle containing 8 g of CS powder. The growth rate of the CS is ~ 1.3 g h^{-1} with a small combustion nozzle having a 1.5 mm orifice tip and an ethylene-oxygen flow ratio of 5:3. The CS growth rate can be further increased with higher flow rates. The density of collected CS is approximately 0.86 g cm^{-3} , which is measured by pressing the CS powder into a CS film using a hydraulic screw press (see the Supporting Information, Figure S1). The as-grown CS has a size range of 5–50 nm (see the Supporting Information, Figure S2). Figure 1c shows a transmission electron microscopy (TEM) image of the CS, which demonstrates typical amorphous carbon structures,³⁵ containing random graphitic striations. As is shown in Figure 1c, the CS particles contain entangled and rippled graphitic striations in the inner cores and on the outer layers, separately. Figure 1d shows a typical Raman spectrum of the CS, with two dominant Raman peaks at 1350 and 1590 cm^{-1} ascribed to the D- and G-bands, respectively.³⁶ The overlapping of D- and G-

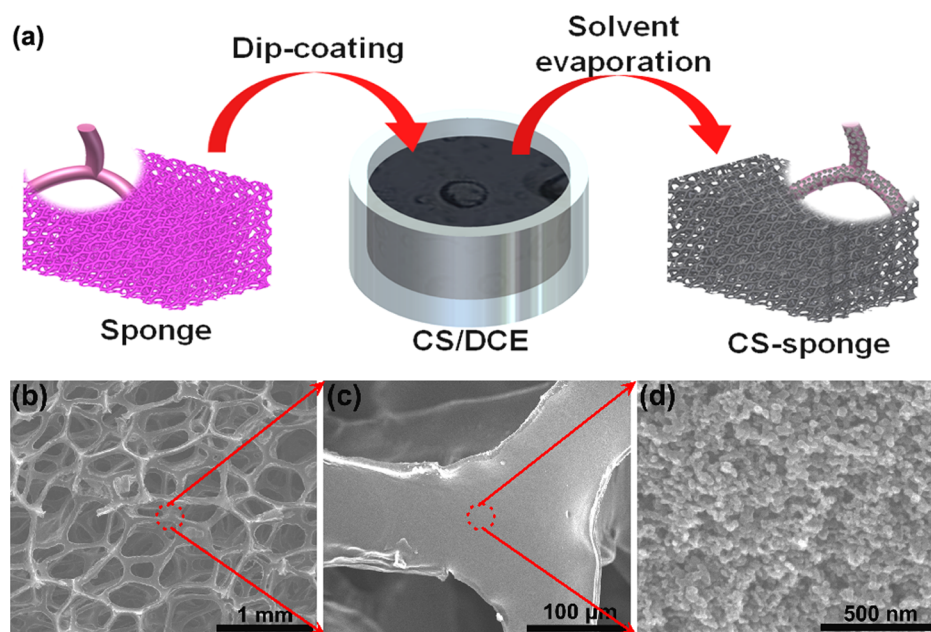


Figure 2. (a) Schematic showing the CS-sponge preparation by dip-coating and (b–d) SEM images of a CS-sponge.

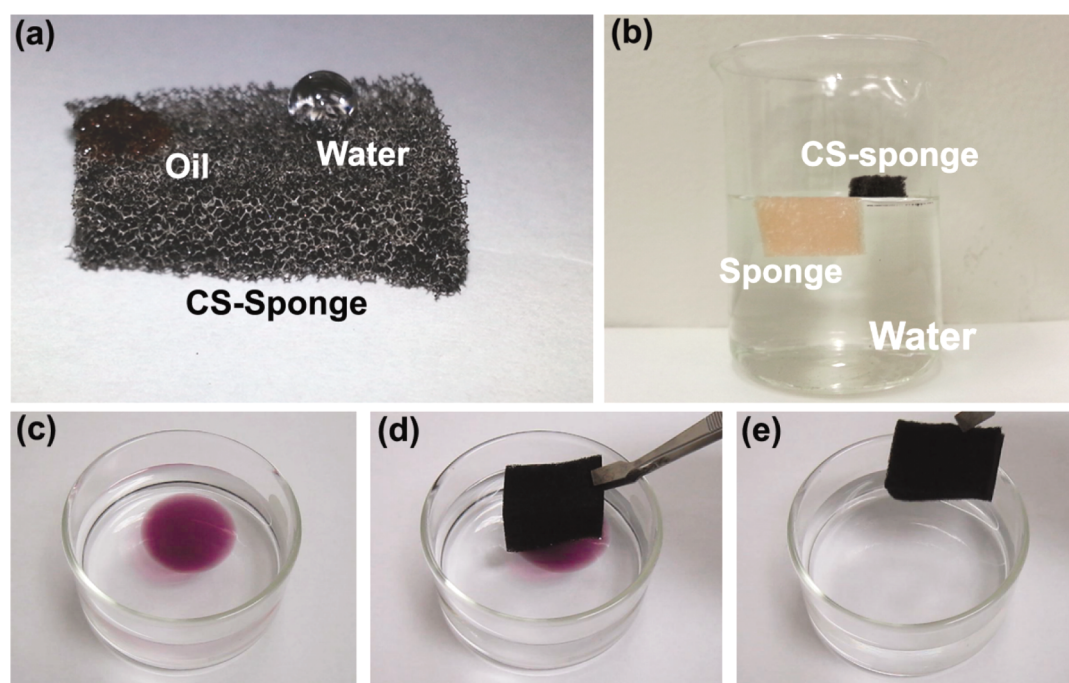


Figure 3. (a) Photograph of water and oil droplets on the surface of a CS-sponge. (b) Photograph of pure and CS-sponges placed on water. (c–e) Photographs demonstrating the removal of an oil droplet from water using a CS-sponge.

bands indicates a low crystallinity of the synthesized CS. The CS powder has a specific surface area of $440 \text{ m}^2 \text{ g}^{-1}$, according to the measurements of the nitrogen adsorption isotherm (see the Supporting Information, Figure S3). The water contact angle of the CS surface is $\sim 140^\circ$ (Figure 1e), indicating superior hydrophobicity.

The CS-sponges were prepared by the dip-coating method,³ as shown in Figure 2a. A $1 \times 1 \times 0.5 \text{ cm}^3$ piece of commercially available melamine sponge was dipped into a CS dispersion in DCE. After evaporation of the DCE by drying the CS-coated sponge in an oven at 80°C for 2 h, the CS was strongly attached to the skeleton of the melamine sponge due to the van

der Waals interactions between the CS and the sponge.³ Parts b–d of Figure 2 show the SEM images of a CS-sponge, which demonstrates a three-dimensional hierarchical porous structure. The pore size of the CS-sponge ranges from 85 to $500 \mu\text{m}$. As shown in Figure 2c and d, the CS was uniformly coated on the skeleton of the sponge, forming a nanoscale porous surface (Figure 2d). The nanoscale porous surface and the hierarchical porous structure synergistically contribute to the hydrophobicity of the CS-sponge and thus provide high efficiency in absorbing oils and organic solvents.^{3,5,37}

The CS-sponge demonstrates high hydrophobicity and oleophilicity, as shown in Figure 3a and b. In Figure 3a, an

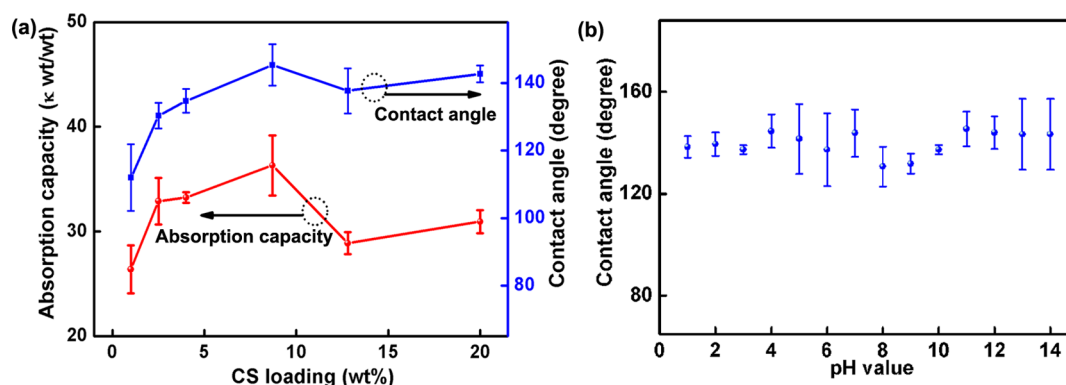


Figure 4. (a) Dependence of the absorption capacity on the CS loadings for pump oil (Varian, Inc.). (b) CAs of the CS-sponges after 12 h of floating on aqueous solutions with pH values from 1 to 14.

engine oil droplet (Evinrude Johnson, TC-W3) was immediately absorbed by the CS-sponge at the moment it was dropped on its surface. In contrast, a water droplet dropped onto the CS-sponge surface can stay on the surface and maintain its spherical shape, indicating the hydrophobic property of the CS-sponge. As shown in Figure 3b, the CS-sponge floated on the surface of the water while an uncoated sponge submerged in the water. Therefore, it is confirmed that the hydrophobic property of the CS-sponge comes from the nanoscale porous surface and the hierarchical porous structure.³⁷ Parts c–e of Figure 3 demonstrate the oil removal of the CS-sponge. When a piece of CS-sponge contacted the oil droplet on the water surface, the sponge absorbed the whole oil droplet in seconds (see the Supporting Information, video clip). Fourier transform infrared (FTIR) spectroscopy was used to analyze the CS-sponge before and after oil absorption. No obvious change was observed in the FTIR spectra (1750–2750 cm^{-1} , see the Supporting Information, Figure S4), which suggests that no chemical reaction occurs in this process, and the physical absorption dominated by capillary force and oleophilicity plays an important role in oil absorption.¹⁷

The performance of the CS-sponge was systematically investigated by measuring the absorption capacity for a broad spectrum of oils and organic solvents. Figure 4a shows the absorption capacity of CS-sponge samples with different CS loadings for pump oil (Varian, Inc., Part Number: P101441). The CS loadings on the sponge can be controlled by a number of dip-coating cycles. As shown in Figure 4a, the absorption capacity of the CS-sponge for the pump oil increases with the CS loading. At a CS loading of ~9 wt % (CS-sponge density: 0.03 g cm^{-3}), the absorption capacity reaches the highest value of ~36 times the CS-sponge weight, which is better than the absorption capacity of CNT-based (Cheaptubes, Inc.) and graphene-based (ACS Materials, Inc.) sponges prepared using the same dip-coating method (see the Supporting Information, Figure S5). The relationship between the water contact angle of the CS-sponge samples and the CS loadings was investigated. As shown in Figure 4a, the contact angle increases with the CS loading. At the CS loading of ~9 wt %, the contact angle reaches the highest value of 144° , indicating a high hydrophobicity for the CS-sponge. As the CS loading is more than ~9 wt %, no obvious change has been observed for the contact angles. The results indicate that the increase of the CS-sponge absorption capacity for pump oil is ascribed to the hydrophobicity enhancement by increasing the CS loading. Unsaturated CS coating (<9 wt %) leads to low absorption

capacity. Oversaturated CS coating (>9 wt %) cannot further improve the hydrophobicity but causes sponge pore blocking and the increase of the CS-sponge weight, resulting in the degradation of the absorption capacity.³ The durability of the CS-sponges (CS loading of ~9 wt %) in corrosive environments was tested by measuring the CAs of the CS-sponges after 12 h of floating on aqueous solutions with different pH values (Figure S6, Supporting Information). As shown in Figure 4b, the average CAs are still greater than 130° after 12 h of floating on aqueous solutions with different pH values, which indicates the potential application of the CS-sponge in oil cleanup even under corrosive conditions.

The absorption capacity of the CS-sponge with ~9 wt % CS loading for different oils and organic solvents was evaluated, as shown in Figure 5a. The CS-sponge demonstrates an absorption capacity in the range of 25–80 times its original weight. The absorption capacity depends on the density and viscosity as well as the surface tension of the oils and organic solvents.⁵ In general, the CS-sponge can have a higher absorption capacity for those oils/solvents with large density and surface tension but low viscosity (see the Supporting Information, Table S1). For example, the highest absorption capacity of the CS-sponge has been achieved for DCE, since it has the highest density among the solutions. Although acetone, methanol, and ethanol have almost the same density ($\sim 0.79 \text{ g cm}^{-3}$), the absorption capacity of the CS-sponge for acetone is higher than that for methanol and ethanol due to the lower viscosity (0.31 cP vs methanol 0.59 cP and ethanol 1.96 cP) and higher surface tension of acetone (0.025 N m^{-1} vs methanol 0.023 N m^{-1} and ethanol 0.022 N m^{-1}). Compared with inorganic nanowire membrane,¹ graphene aerogel,⁴ and polydimethylsiloxane sponge,⁸ the CS-sponge has a higher absorption capacity for various oils and organic solvents (Figure 5b). Despite the relatively lower absorption capacity than that of graphene sponge³ and graphene-CNT hybrid foam,⁵ the procedures to produce CS and prepare CS-sponge are simple, cost-effective, and scalable.

In the application of contaminant removal, both large absorption capacity and high recyclability are required. The recyclability of the CS-sponge is shown in Figure 6. In the recycling experiments, the absorbed pump oil was extracted from the CS-sponge using an acetone rinse. The CS-sponge was subsequently dried at 100°C . The absorbed organic solvents (DCE, toluene, and acetone) were removed by directly heating the CS-sponge at 140°C in a fume hood. As shown in Figure 6, the absorption capacity of the CS-sponge does not

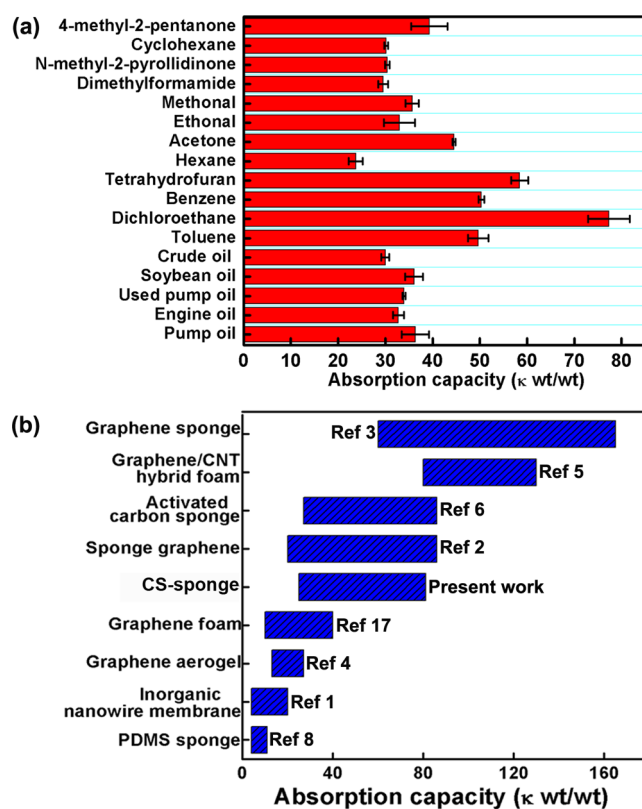


Figure 5. (a) Absorption capacity of the CS-sponge for various oils and organic solvents. (b) Comparison of the absorption capacity of different absorbents.

show severe degradation after 10 cycles, indicating a highly stable absorption performance. After 10 cycles, approximately 94% of the initial oil absorption capacity is kept for the CS-sponge (Figure 6), which is much higher than that of the CS-sponge recovered by manual squeeze (Figure S7, Supporting Information). The decrease in the oil absorption capacity of the CS-sponge could be ascribed to the weight and hydrophobicity changes of the CS-sponges after a couple of recycles of absorption (Figure S8, Supporting Information). As the interaction between the CS and the sponge (van der Waals) is weak, approximately 3% weight loss was observed for the CS-sponge after 10 cycles. Meanwhile, its CA was reduced to 120° (Figure S8, Supporting Information), suggesting a reduction of the hydrophobicity of the CS-sponge. With the further increase of the cycle number to 20, the CS-sponge demonstrates 6% weight loss with a CA less than 90° (Figure S8, Supporting

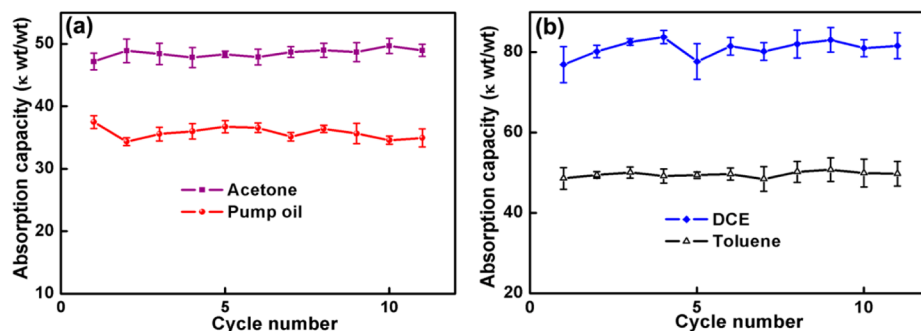


Figure 6. Absorption recyclability of the CS-sponges.

Information), indicating that the CS-sponge surface became hydrophilic.

4. CONCLUSIONS

In conclusion, CS-sponge for use in oil contaminant cleanup has been developed in this study. The CS synthesis and CS-sponge preparation procedures are simple, cost-effective, and scalable. The absorption investigation demonstrates that the CS-sponge is highly efficient and stable in absorbing a wide range of oils and organic solvents. It has a large absorption capacity of up to 80 times its original weight, along with high recyclability of more than 10 times. The results suggest that the CS-sponge is a promising material for use in environmental remediation to remove oils from water.

■ ASSOCIATED CONTENT

Supporting Information

Video clip showing oil absorption by a CS-sponge, nitrogen adsorption/desorption isotherm of CS, and Fourier transform infrared spectroscopy analyses of CS-sponges, as well as density, viscosity, and surface tension values of organic solvents for the absorption experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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