

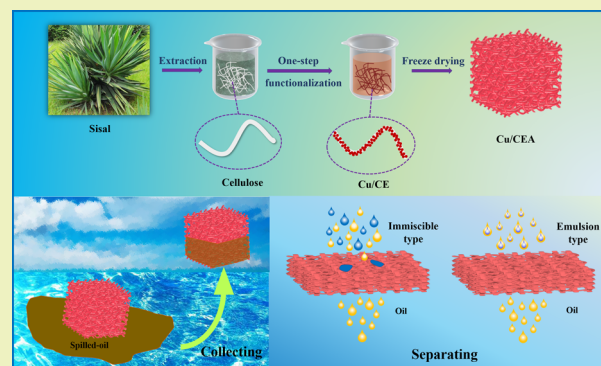
Sustainable, Flexible, and Superhydrophobic Functionalized Cellulose Aerogel for Selective and Versatile Oil/Water Separation

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S Supporting Information

ABSTRACT: Aerogels, as ultralight three-dimensional (3D) highly porous materials, show great superiority in oil and organic pollutant cleanup. Notably, biomass aerogels have also attracted wide interest due to the advantages of huge reserves, low cost, renewability, biodegradation, and nontoxicity to the environment. Herein, a sustainable, flexible, and superhydrophobic functionalized cellulose aerogel, copper nanoparticles-coated cellulose aerogel (Cu/CEA), is reported. The hydrophobic Cu/CEA was simply fabricated by one-step depositing Cu nanoparticles coating on the cellulose fibers extracted from renewable natural sisal in liquid phase followed by freeze-drying. The hydrophobic functionalization approach is facile, cost-effective, and suitable for large-scale production and environmental friendliness, without additional organic hydrophobic modification. The highly porous Cu/CEA as absorbent can selectively and quickly collect oily contaminant, exhibiting high oil absorption capacity and rate, and good recyclability. In addition, it can also act as a thick film to continuously and rapidly separate oil/water mixtures including emulsions, possessing very high separation efficiency and flow rate. Hence, the versatile and high-performance functionalized cellulose aerogel possesses a promising practical application in oily wastewater treatment and pollution remediation.

KEYWORDS: Cellulose aerogel, Superhydrophobicity, Oil/water separation, One-step functionalization, Nonorganic hydrophobic modification



■ INTRODUCTION

The increasing discharge of industrial oily wastewater and frequent occurrence of oil-spill accidents not only cause serious damage to the ecological environment, but also lead to huge waste of valuable resources of oil and purified water.^{1–3} Therefore, achieving effective separation of oil/water mixtures is extremely imperative to the sustainable development of humanity and nature.^{4,5} The advanced hydrophobic porous absorbent materials, by effectively absorbing oily target mixed in an aqueous phase, show many advantages such as high absorption speed, high separation efficiency and reused performance, and compatibility with large-area application, which have made them ideal potential candidates.^{6,7}

Aerogels, a promising kind of porous material, have attracted tremendous interest in many applications owing to their prominent and advanced properties, such as ultralight network structure, high porosity, large specific surface area, and strong rigidity.^{8,9} To date, various aerogels such as synthetic silicon,¹⁰ CNT,¹¹ graphene,¹² and biomass materials^{13–15} have been widely investigated and shown great potential in oil-spill cleanup and water environmental recovery. Due to the mechanical brittleness of pure silica aerogels, they are not able to withstand the capillary force and crack seriously during the absorption process, and absorbents with oil are difficult to

recycle. For CNT or graphene aerogels, many shortcomings such as expensive precursors, complicated preparation process, or the need of complex equipment hamper their large-scale production in practical applications. The biomass-based materials from natural plants and animal residues, by contrast, have greater advantages of inexhaustible renewable source, renewability, biodegradability, low cost, and security.^{16,17} Cellulose, as one of the most abundant biomass materials, due to its high strength and stiffness, is an ideal base material for the preparation of aerogels, and the resultant cellulose-based aerogels have been widely researched and applied in oil pollutant treatment.^{18–20}

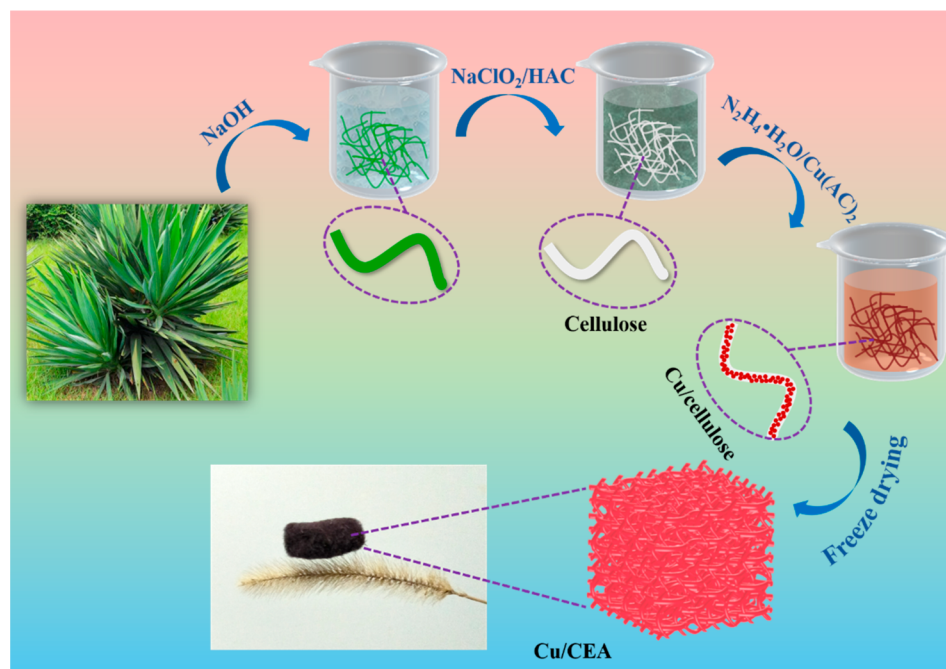
It is well-known that oil absorption performance of absorbents depends not only on the density and porosity, but also largely on the surface wetting property and capillary effect.²¹ Thus, based on native cellulose with amphiphilicity, the cellulose-based aerogels should be endowed with special wettability of hydrophobic and oleophilic properties to improve the selectivity for oil/water.^{22,23} Generally, the numerous reported hydrophobic surfaces were prepared by

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Scheme 1. Fabrication Process of Functionalized Cellulose Aerogel



first fabricating rough microstructure and then modifying with hydrophobizing agents with low-surface energy, which are usually tedious and complex. Yuan et al.²⁴ fabricated superhydrophobic cellulose-based carbon@SiO₂@MnO₂ aerogel by sol–gel process, high-temperature carbonization, and hydrothermal reaction to obtain rough microstructure, and finally organic hydrophobic modification. Obviously, this preparation process is quite complicated, high-cost, and ecologically unfriendly. Moreover, the common hydrophobization approaches include chemical vapor deposition (CVD),^{25–27} cold plasma treatment,^{28,29} and atomic layer deposition (ALD) methods to graft low-surface-energy alkyl or fluorine functional groups.^{19,30} However, the organic modifiers, especially fluoroalkylsilane, are expensive and harmful to the environment. Furthermore, these hydrophobic techniques usually need extra energy and specific operating equipment and accurate control of preparation conditions. These problems limit the large-scale production of hydrophobic cellulose-based aerogels.³¹ Therefore, it is imperative to develop a facile and economical method of massively fabricating hydrophobic cellulose aerogels.

Sisal as nearly the most consumable and extensively tough fiber crop in the present world; it is so rich in cellulose fiber that it could be used as an ideal raw material for extraction of cellulose. Herein, we report a facile route to prepare superhydrophobic functionalized cellulose-based aerogel by using natural sisal as a raw material. The functionalization process was performed by one-step depositing of Cu nanoparticles coated on the surface of cellulose fiber in aqueous phase at room temperature without additional equipment or energy input, which directly achieved a hydrophobic surface without further organic hydrophobic modification. For the hydrophobization of cellulose-based aerogel, this approach is a more cost-effective and simple method than previous reports. Notably, the obtained functionalized cellulose aerogel can quickly collect oily contaminant and continuously separate various oil/water mixtures including

emulsions, showing excellent performance. The superhydrophobic and biodegradable functionalized cellulose aerogels would be ideal novel candidates for versatile treatment of oil spills and remediation of oily wastewater in the practical world.

EXPERIMENTAL SECTION

Materials. Sodium chlorite (NaClO₂), copper acetate monohydrate (Cu(CH₃COO)₂·H₂O), hydrazine hydrate (N₂H₄·H₂O, 80%), acetic acid (CH₃COOH, 36%), and sodium hydroxide (NaOH) were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sisal leaves were collected from the campus of Jiangsu University (Zhenjiang, China). Deionized water (DI water) was used in all the experiments. All the above chemicals were used as received without any further purification.

Extraction of Biomass Cellulose. The biomass cellulose was obtained by soaking in alkali solution to remove hemicellulose, lignin, and other components of sisal leaves. Typically, the raw sisal leaves were chopped and then cleaned up with DI water. Ten grams of the pretreated sisal leaf fragments were immersed in 500 mL of NaOH solution (5 wt %) under stirring for 4 h at 70 °C. The obtained raw sisal cellulose was washed with DI water, followed by ethanol, several times to remove the residual impurities. Subsequently, a desired amount of raw cellulose fibers was immersed into 200 mL of solution containing 2 wt % NaClO₂ and 1.5 mL acetic acid, and then held with stirring at 60 °C for 3 h to obtain a white cellulose sol suspension. The pH value was controlled at approximately 7 by washing with DI water. Finally, purified sisal cellulose was obtained after being dried in a vacuum oven at 60 °C for 12 h. The biomass cellulose extraction process is presented in Scheme 1.

Functionalization Process. The functionalized cellulose was fabricated by a simple one-step dipping method of the chemical reduction of copper acetate by hydrazine hydrate. In a typical procedure, 5 g of above as-prepared cellulose fibers was well-dispersed in 100 mL of aqueous solution containing 5 mmol of copper acetate monohydrate, and then 4.0 mL of hydrazine hydrate (80%) was dropwise added into above mixture solutions and kept for 12 h at room temperature to obtain Cu/CE. Subsequently, the Cu/CE was taken out and washed with DI water through filtration, followed by drying in a vacuum oven at 60 °C for 6 h. The functionalization process of cellulose is shown in Scheme 1.

Preparation of Functionalized Cellulose Aerogel. The functionalized cellulose aerogel was prepared by simple freeze-drying technology. Typically, the as-prepared Cu/CE was dispersed in 20 mL DI water under vigorous stirring for 2 h at room temperature to form the homogeneous suspension, and the mass concentration of functionalized cellulose in aqueous dispersion was controlled with 0.4, 0.6, 0.8, and 1.0 wt %, respectively. Afterward, the suspension was poured into a mold and then frozen at -20°C for 24 h and then dried in vacuum at -53°C and 0.113 mbar for 72 h to obtain the Cu/CEA. The preparation process of functionalized cellulose aerogel is illustrated in Scheme 1.

Density and Porosity of Functionalized Cellulose Aerogel. The density (ρ_A) and porosity (ϕ) of functionalized cellulose aerogel can be calculated by

$$\rho_A = \frac{m_A}{V_A} \quad (1)$$

where m_A and V_A are the mass and volume of the cylinder-shaped Cu/CEA, respectively.

$$\phi = \left(1 - \frac{\rho_A}{\rho_S}\right) \times 100 \quad (2)$$

where ρ_A is the bulk density of Cu/CEA and ρ_S is the density of solid scaffold (i.e., functionalized cellulose fibers). The density of solid scaffold was estimated as follows:

$$\rho_S = \frac{1}{\left(\frac{m_c}{\rho_c} + \frac{m_{Cu}}{\rho_{Cu}}\right)} \quad (3)$$

Where m_c is the mass of cellulose and ρ_c is the density of cellulose (1.5 g/cm^3); m_{Cu} and ρ_{Cu} are the mass and density (8.9 g/cm^3) of copper nanoparticles coating deposited on the surface of cellulose fibers, respectively.

Characterization. The surface morphologies and elements of the obtained cellulose-based aerogels were observed by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4800) equipped with energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD, 6100Lap) was used to analyze the crystal structures of different samples in the 2θ range from 10° to 80° with a scanning rate of $4^{\circ}/\text{min}$. The surface chemical property of as-prepared samples was identified by X-ray photoelectron spectrometer (XPS, VG Multilab 2000). Fourier transform infrared spectra (FT-IR) analysis was performed in the range of $400\text{--}4000 \text{ cm}^{-1}$ using a FT-IR spectrophotometer (Thermo Nicolet, NEXUS, TM) equipped with ATR accessory to identify functional groups of samples. The contact angle goniometer (KSV CAM 101) was used to measure the contact angle of as-prepared samples at ambient temperature and the volume of probing liquids was about $5 \mu\text{L}$. The water concentration of the purified filtrates was analyzed using Karl Fischer Titrator (Mettler Toledo DL31, Switzerland).

Oil/Water Separation Performance. For the oil absorption test, the weight of the as-prepared functionalized cellulose aerogels with different mass concentration was measured before absorbing oil. Afterward, the samples were immersed into certain oils or organic solvents for some time to reach the absorption saturation and then taken out from the liquid bath. Then, the absorption-saturated samples were gently wiped with filter paper to remove unabsorbed liquids, followed by quick weighing. The absorption capacity, Q_r (g/g), of obtained aerogels was calculated by the following equation:

$$Q_r = \frac{M_a - M_b}{M_b} \quad (4)$$

where M_b and M_a are the masses of aerogels before and after absorption, respectively.

To determine the absorption kinetics, the as-prepared equal-sized samples functionalized cellulose aerogels with different mass concentration were immersed into the *n*-hexane bath at different

time to measure their weight change, respectively. The kinetic constant, k_1 , was calculated by the following equation:

$$\ln \frac{Q_s}{Q_s - Q_t} = k_1 t \quad (5)$$

where Q_s and Q_t are finally saturated absorption capacity and absorption capacity at specific time t .

For the separation of oil/water mixtures (including immiscible mixtures and emulsified mixtures), the as-prepared functionalized cellulose aerogels (35 mm in diameter, 20 mm in height) with a specific mass concentration were fixed on the filtering apparatus. The oil/water mixtures were poured in the aerogel membrane and then separated by gravity only. For the immiscible oil/water mixtures, the separation efficiency, S_e (g/g), could be determined by the following equation:

$$S_e = \frac{m_1}{m_o} \times 100\% \quad (6)$$

where m_o and m_1 are the weight of original water before separation and that of water after separation.

For the water-in-oil emulsions, the separation efficiency, S_e , was determined by the following equation:

$$S_e = \frac{C_o - C_a}{C_o} \times 100\% \quad (7)$$

Where C_o and C_a are the water content in the original emulsions and collected filtrates after separation.

The adsorption–distillation approach was applied to evaluate the recyclability of functionalized cellulose aerogel with different mass concentrations. Trichloromethane was chosen as the oil model for recycling (the boiling point of $\sim 62^{\circ}\text{C}$). Typically, the oil-adsorbed functionalized aerogel was placed in a flask in an atmospheric distillation unit and heated at 65°C until the adsorbate stopped flowing out. The dried recycled aerogel was taken out from the flask and then used for further cyclic absorption. The absorption capacities of functionalized cellulose aerogel with different mass concentrations were all calculated by eq 4 after each cycle. The recycling process by adsorption–distillation approach is illustrated in Figure S1.

RESULTS AND DISCUSSION

Morphology and Composition Characterization. The cellulose-based aerogels possess excellent handleability. Diverse shape and size of as-prepared Cu/CEAs could be controlled by using molds. The different mass concentration of Cu/CEAs could be adjusted by controlling the amount of aqueous solvent. Figure S2 shows the SEM images of Cu/CEAs with different mass concentration of 0.4 wt % (a), 0.6 wt % (b), 0.8 wt % (c), and 1.0 wt % (d), respectively, which present a cylinder with a diameter of 16 mm and height of 20 mm. It can be seen that the obtained Cu/CEAs have a porous and interconnected 3D network structure which formed by self-assembled mechanical entanglement of cellulose-based fibers and the length of the single fiber ranges from hundreds of micrometers to a few millimeters. The highly porous and well-organized structures endowed the functionalized biomass aerogels with high liquid absorption capacities and flow properties. Meanwhile, the increase of the functionalized cellulose fibers causes the denser structure and smaller pore size. The specific property parameters of Cu/CEAs with different mass concentration are summarized in Table 1.

It is well-known that the surface wettability of a material is largely determined by micromorphology structure and chemical composition that could be characterized by SEM images and EDS analyses. Figure 1a–d shows the low- and high-magnification SEM images of pristine sisal cellulose

Table 1. Property Parameters of As-Prepared Functionalized Aerogels with Different Mass Concentration

aerogels	concentration (wt %)	density(mg/cm ³)	porosity (%)
a	0.4	4.56 ± 0.31	99.76
b	0.6	7.13 ± 0.26	99.54
c	0.8	9.31 ± 0.44	99.43
d	1.0	11.23 ± 0.28	99.25

aerogel (a-b) and Cu/CEA (c-d), respectively. The low- (Figure 1a) and high- (Figure 1b) magnification SEM images of pristine cellulose aerogel show that the sisal cellulose fiber is about 5 μm in diameter and the surface is relatively smooth. The surface micromorphology of functionalized cellulose aerogel by Cu nanoparticles coating the cellulose fibers is shown in Figure 1c. It can be seen that the smooth cellulose fiber is covered with Cu nanoparticles with particle size ranging 50–200 nm to fabricate rough micro/nanostructure, which provides the structural basis of hydrophobicity.

The surface chemical composition of Cu/CEA and distribution of coating were determined by using energy dispersive X-ray spectroscopy (EDS). Figure 1e shows that peaks of C, O, and Cu elements could be observed in the elemental analysis spectrum and mainly dominated by Cu,

followed by lower proportion of C and O (the signal of Au element is from the gold spray). The corresponding SEM-EDS mapping images are presented in Figure 1f: the homogeneous and complete distribution of Cu nanoparticles can be seen coated on the surface of cellulose fiber, suggesting that it is effective and helpful to fabricate compact copper coating via the one-step dipping process of the chemical reduction of copper acetate by hydrazine hydrate. The element Cu is completely obtained from copper coatings, and a relatively smaller amount of elemental C should be from the cellulose substrate. In addition, the similarly small amount of element O could be related to the cellulose substrate and even the oxidation of Cu nanoparticle coating.

X-ray photoelectron spectroscopy (XPS) was implemented to further determine the near-surface elemental composition and the chemical state of as-obtained cellulose aerogels. Figure 2A shows the full-survey-scan spectrum of as-prepared pristine cellulose aerogel (a) and functionalized cellulose aerogel (b). Compared to the curves of (a), obvious sharp peak of Cu element appears but the peak strength of C and O elements becomes weak in the curve of (b), which would be ascribed to the effect of copper coating on cellulose fiber substrate. To further assess the purity of Cu nanoparticles coated on the surface of Cu/CEA, the high-resolution Cu 2p spectrum is

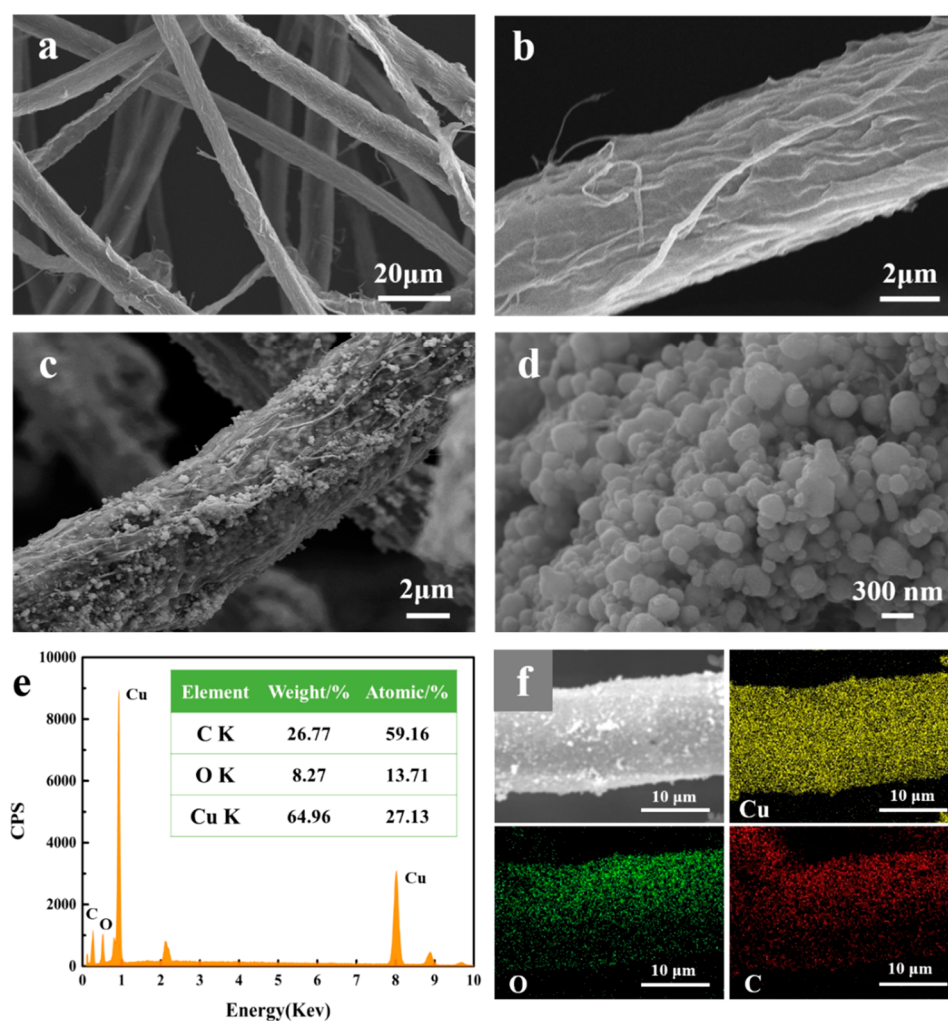


Figure 1. SEM images of pristine sisal cellulose aerogel (a-b) and Cu/CEA (c-d) at different magnification; EDS spectrum (the inset is element analysis) (e) and SEM-EDS elemental mapping of Cu/CEA (f).

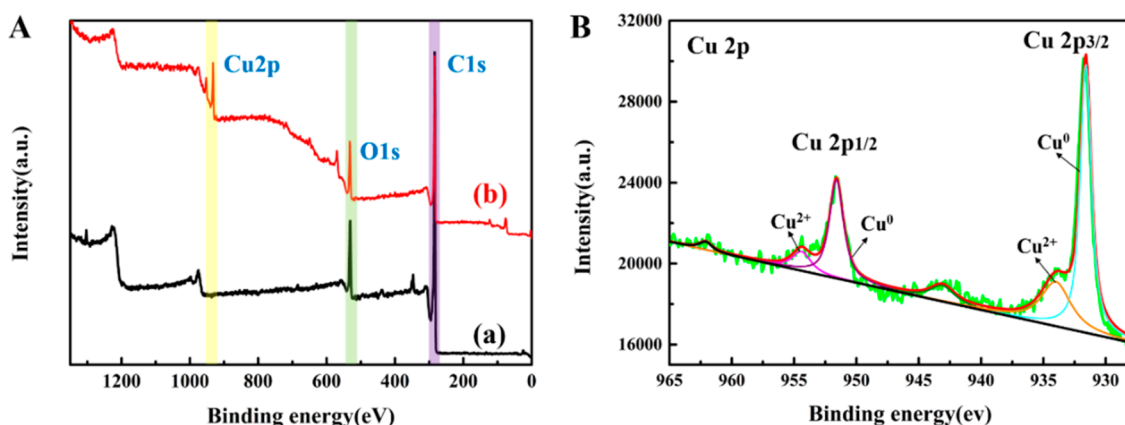


Figure 2. XPS spectra (A) of pristine cellulose aerogel (a) and Cu/CEA (b), and high-resolution Cu 2p spectrum (B) of Cu/CEA.

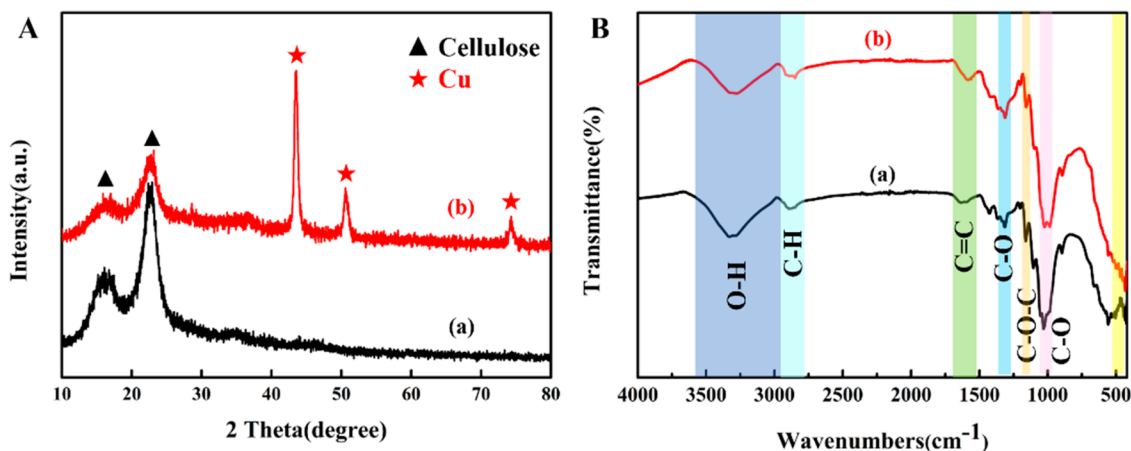


Figure 3. XRD patterns (A) and FT-IR spectra (B) of cellulose aerogel (a) and Cu/CEA (b).

shown in Figure 2B. The major peaks at 931.6 and 951.6 eV in spectra are assigned to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. These two peaks could be decomposed into two groups of Cu⁰ (binding energy = 931.5 and 951.5 eV) and Cu²⁺ (binding energy = 934.1 and 954.3 eV) species. Moreover, two small peaks at 943.0 and 962.1 eV are observed, which should be attributed to shakeup satellite peaks of CuO. The results show that the Cu nanoparticles coating of the Cu/CEA surface could be oxidized after exposure to open environment for some time, so that a small minority of pure copper was oxidized to copper oxide. However, obviously, the main peaks of Cu²⁺ and shakeup satellite peaks of CuO are much weaker than characteristic peaks of Cu⁰, suggesting that the degree of oxidation is extremely low and the content of CuO is very small.

X-ray diffraction (XRD) patterns of the pristine cellulose aerogel and functionalized cellulose aerogel are shown in Figure 3A. The curve (a) is the XRD pattern of original cellulose aerogel. It can be seen that two characteristic peaks at $2\theta = 16.9^\circ$ and 22.7° correspond to (110) and (020) lattice planes of cellulose, respectively, which are also observed in the curve (b) that is the XRD pattern of Cu/CEA. Moreover, the XRD pattern of Cu/CEA shows three strong sharp peaks at $2\theta = 43.3^\circ$, 50.5° , and 74.2° , attributed to (111), (200), and (220) crystalline planes of pure metallic copper, respectively, demonstrating that the surface of pristine sisal cellulose was successfully coated Cu nanoparticles and the cellulose crystalline structure was still preserved during the functional-

ization treatment. Remarkably, no additional diffraction peaks, such as characteristic diffraction peaks of CuO or Cu₂O, are found in the XRD pattern of Cu/CEA, indicating quite high chemical purity and stability of the copper coating. However, the analytical result is not strictly consistent with the XPS analysis of slight oxidation occurring on the surface of Cu nanoparticle coating. Because of the diversity of different analytical technology and measuring environment, this result is normal and understandable. Therefore, the high purity of elementary Cu is helpful to significantly improve the hydrophobicity of functionalized cellulose aerogel.

To investigate the transformation from pristine cellulose aerogel to functionalized cellulose aerogel, the Fourier transform infrared (FT-IR) spectra were shown in Figure 3B. Many main characteristic absorption bands of cellulose, such as 3328 cm^{-1} (–OH), 2890 cm^{-1} (C–H stretching), 1636 cm^{-1} (C=C stretching), 1427 cm^{-1} (C–H bending), 1314 cm^{-1} (C–O stretching), 1158 cm^{-1} (C–O–C stretching), and 1025 cm^{-1} (C–O bending), are detected in the spectra of pristine cellulose aerogel (a) and Cu/CEA (b), which are attributed to the typical functional groups of cellulose. In addition, from the comparison of the two spectra, a broad absorption band at $300\text{--}500\text{ cm}^{-1}$ (marked with yellow stripe) is detected at the spectrum of Cu/CEA (b), which could be assigned to the effect of between copper coating and cellulose.

Surface Wettability. The special wettability of materials is important for selective separation of oil/water mixtures. Figure 4 shows the special wettability of pristine cellulose aerogel and

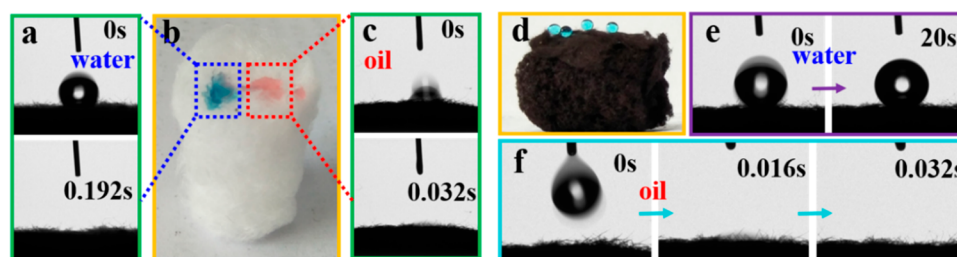


Figure 4. Surface wettability of pristine cellulose aerogel (the sequential WCA photographs (a), the optical image of drops of water and oil on the surface (b), and the sequential OCA photographs (c)) and Cu/CEA (the optical image of water drops on the surface (d), the sequential WAC photographs (e), and the sequential OCA photographs (f)). Water was dyed with methylene blue and pump oil was dyed with Sudan III.

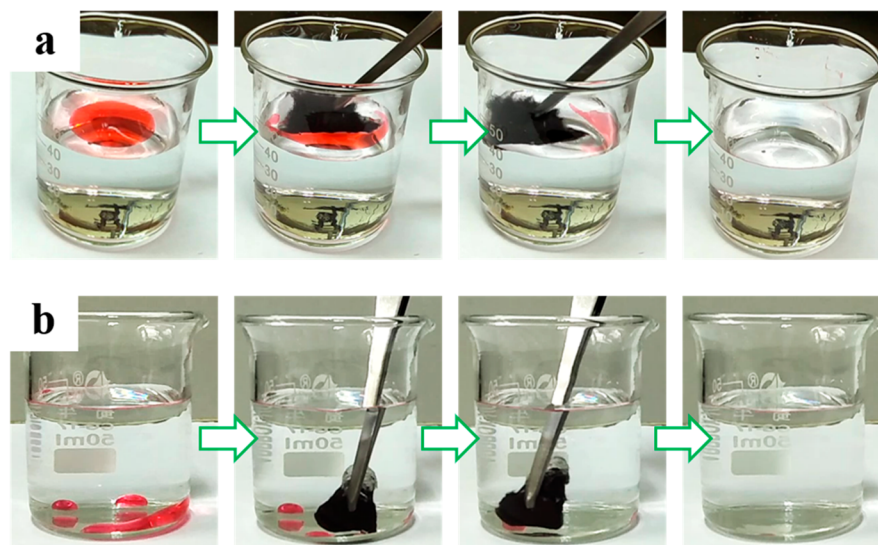


Figure 5. Removal of *n*-hexane (a) and trichloromethane (b) dyed with Sudan III from the surface and bottom of water with a piece of Cu/CEA.

functionalized cellulose aerogel. The specific measurement was performed by using a contact angle goniometer to evaluate their hydrophobic and oleophilic properties. For the pristine cellulose aerogel obtained directly from sisal cellulose fibers, the surface can be completely wetted and permeated by water and oil, leaving blue water mark and red oil mark (Figure 4b). Figure 4a shows that a water droplet rapidly penetrated the cellulose aerogel in 0.192 s, and Figure 4c shows that an oil droplet more quickly penetrated the cellulose aerogel in 0.032 s, which indicates that the pristine cellulose aerogel possesses the amphipathicity of hydrophilicity and oleophilicity. Thus, the cellulose aerogel does not have wetting selectivity and is not suitable for oil/water separation. To achieve the goal of a hydrophobic surface, the cellulose fibers were functionalized by rough Cu nanoparticles coated with low-surface energy to obtain Cu/CEA. The microstructure and chemical constitution foundations of hydrophobicity are confirmed by the above analyses of morphology and composition characterization. Figure 4d shows that blue water droplets remain spherical on the Cu/CEA. By the contact angle measurement, the water droplet maintains its original shape well without obvious penetration above 20 s and the water contact angle (WCA) is 150.3°, showing prominent water repellency (Figure 4e). Meanwhile, an oil droplet fully and quickly penetrated the Cu/CEA under capillary force in less than 0.032 s. These results indicate that Cu/CEA possesses superhydrophobic and superoleophilic properties.

Due to the superhydrophobicity and superoleophilicity, the as-prepared functionalized cellulose aerogels are potential candidates for separation of oils and organic solvents from water. As shown in the Figure 5a (and Video S1), when the Cu/CEA was placed into the *n*-hexane/water mixture, *n*-hexane floating on the water was completely and quickly absorbed less than 10 s, leaving the clean water. Moreover, as shown in Figure 5b (and Video S2), the Cu/CEA can selectively absorb trichloromethane rather than water from the bottom of water in 7 s. Therefore, the as-obtained Cu/CEAs could be an ideal absorbent for treatment of oil-spill and remediation of oily wastewater.

Due to the surface wettability determining the selectivity of oil/water separation, the stability of wettability is a crucial factor in practical application. As shown in Figure S2, the stability and durability of hydrophobic surface based on Cu coating were tested by evaluating the WCA changes of functionalized cellulose aerogel for solutions with different pH (a) and NaCl concentration (b), after storing at ambient temperature for a certain time (c) and repeatedly recycling for oil/water separation (d). As can be seen, the WCAs have no very remarkable change when the functionalized cellulose aerogel was at different test conditions, showing the Cu coating on the surface possesses certain chemical stability and durability. Moreover, as shown in Figure S3, the Cu nanoparticle coating on the surface of fiber surface suffers no apparent destruction or peeling and the WCA is about 151.2°

Table 2. Comparison of Different Modification Methods of Reported Cellulose-Based Aerogel

materials	hydrophobic modification	modifier	WCA	cost ^a	ref
Ultralight cellulose-based aerogel	Plasma treatment and soaking	Octadecyltrimethoxysilane	156°	××	29
Nanocellulose aerogel	ALD	TiO ₂	/	××	25
Cotton cellulose aerogel	CVD	Methyltrimethoxysilane (MTMS)	142.8°	××	32
Nanocellulose aerogel	CVD	Octyltrichlorosilane	150°	×	27
Microfibrillated cellulose aerogel	Immersion modification	Methyltriethoxysilane (MTES)	151.8°	✓	23
MTMS-coated cellulose aerogel	Steam modification	MTMS	145°	✓✓	19
Cu/CEAs	RT aqueous phase reaction	Cu nanoparticles	150.3°	✓✓	This work

^a××, high; ×, relatively high; ✓, relatively low; ✓✓, low.

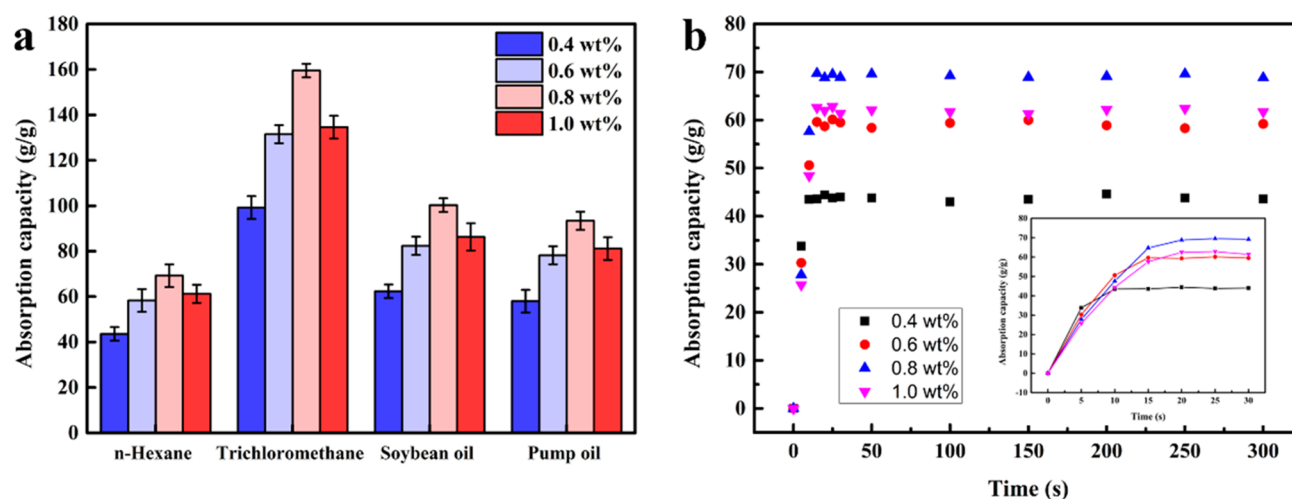


Figure 6. Absorption capacities for four kinds of solvents (*n*-hexane, trichloromethane, soybean oil, and pump oil) (a), and absorption kinetics for *n*-hexane (b) of CEAs with different mass concentration.

after high-temperature calcination at 400 °C in N₂ atmosphere, indicating the fine fastness between coating and fiber surface.

As shown in Table 2, by contrast, the hydrophobization method in this work is more cost-effective and facile than previously reported cellulose-based aerogels.^{19,23,25,27,29,32} The hydrophobicity was achieved by directly using Cu nanoparticles functionalized in aqueous phase at room temperature (RT) without any specific equipment, extra energy, or use of organic modifier. Notably, at the same time to obtain coating with low surface energy, a rough microstructure was also achieved, so the functionalized aerogel possesses bigger WCA (or better hydrophobic performance) than only organic modification.¹⁸ Therefore, this work presented a new perspective and research idea for the hydrophobization method of cellulose-based aerogels, which has great potential in fundamental research and practical applications.

Mechanical Properties. The mechanical properties of absorbents are important for practical applications in order to achieve recyclability. The content of cellulose is a crucial factor for the mechanical properties for as-prepared Cu/CEAs in this work. The effect of cellulose content on mechanical properties of Cu/CEAs with different cellulose contents could be evaluated by a series of compression tests. As can be observed from the compressive stress–strain curves shown in Figure S5, the compressive stresses of aerogels with cellulose content of 0.4, 0.6, 0.8, and 1.0 wt % are 0.03, 0.04, 0.066, and 0.105 MPa at 90% strain, respectively, indicating higher compressive strength of aerogels with high cellulose content. Besides, the Cu/CEAs with different cellulose content were subjected to successive cyclic compress–release measurements. As can be seen from Figure S6, when Cu/CEAs were compressed into

40% of their original height, the heights of four Cu/CEAs were all reduced during several compress–release cycles, while the decrease in relative height is gradually reduced with the increase of cellulose content (from Figure S2a–d). The height of 0.8 and 1.0 wt % Cu/CEAs can recover more than 90% of their original height after repeating many compression–release cycles, exhibiting relatively excellent compressive and flexible properties. From these results, it can be found that recoverability of functionalized aerogels is related to the content of cellulose, and is enhanced with the increase of cellulose content, which could be attributed to the skeleton strength of functionalized aerogels with network structure is enhanced by more cellulose fibers entanglement. Therefore, the better mechanical properties of Cu/CEA are ascribed to its interconnected 3D porous structure with higher density.

Performance of Oil/Water Separation. The effect of cellulose content (0.4, 0.6, 0.8, and 1.0 wt %) on the absorption capacities of Cu/CEAs for four kinds of solvents (*n*-hexane, trichloromethane, soybean oil, and pump oil) is shown in Figure 6a. As can be seen, with the increase in the cellulose content from 0.4 wt % to 1.0 wt %, the absorption capacities for four kinds of solvents all increase first and then decrease, reaching the maximum at the cellulose content of 0.8 wt %. Commonly, the absorption capacity relies on the porosity of as-prepared aerogels, and increases with increase of porosity. However, as derived from Table 1, 0.4 wt % Cu/CEA possesses the highest porosity, while it has minimal absorption capacity. Figure S7 shows the shape change of as-prepared Cu/CEAs after absorption saturation. It can be seen that 0.8 and 1.0 wt % Cu/CEAs have no obvious change, keeping the original cylinder shape, while the Cu/CEA with low mass

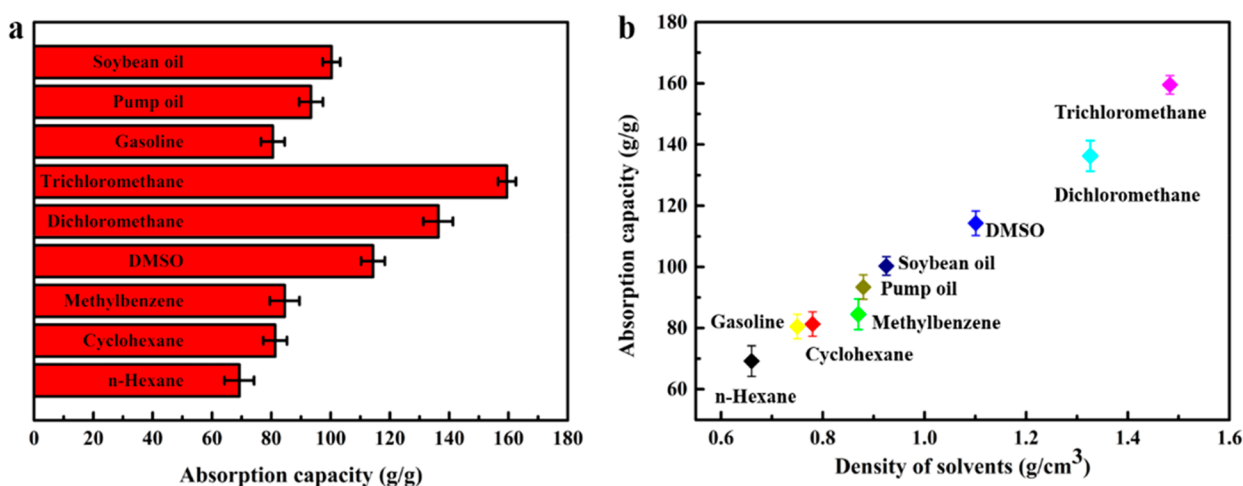


Figure 7. Absorption capacities of CEAs with mass concentration of 0.8 wt % for various oils and organic solvents (a) and absorption capacities marked with density of solvents (b).

concentration of 0.6 wt % collapses significantly. The major reason may be that mechanical properties of 0.4 wt % Cu/CEA and 0.6 wt % Cu/CEA are relatively poor enough to support the porous network structure under the effect of capillary force and lead to disruption, during the process of quickly absorbing solvents. Thus, the smaller size reduces the porosity, which in turn decreases the amount of absorbed solvents. At the mass concentration of 0.4–0.8 wt %, the absorption capacities increase with reduction of deformation; nevertheless, when the shape of saturated Cu/CEAs has no obvious change at the mass concentration of 0.8–1.0 wt %, the absorption capacities decrease with decline of porosity caused by the increase of cellulose content. Therefore, the absorption capacity of the functionalized cellulose aerogel should be the result of interaction between porosity and mechanical properties. These results indicated that the appropriate mass concentration for absorbents is important to effectively improve the absorption capacities, and the 0.8 wt % Cu/CEA has the highest absorption capacity.

The absorption kinetics for *n*-hexane of Cu/CEAs with different mass concentration are shown in Figure 6b. The as-obtained Cu/CEAs all have high absorption speed and the saturations are achieved after less than 25 s. In the detailed graph, the Cu/CEAs with different mass concentration have different absorption rates, and the absorption kinetic constants could be obtained by fitting the results according to the pseudo first-order model (eq 2). The fitting results are shown in Figure S4 and Table S1, in which the kinetic constants of 0.4, 0.6, 0.8, and 1.0 wt % Cu/CEAs are 0.283, 0.164, 0.145, and 0.119 s⁻¹, respectively. These results indicate that oil absorption rates of as-prepared functionalized aerogels are related to the mass concentration, decreasing with the increase in the cellulose content from 0.4 wt % to 1.0 wt %. Overall, though, the as-prepared functionalized aerogels with high porosity and low density have such a high absorption rate that the effect of mass concentration on absorption speed can be negligible.

As shown in Figure 6a, the Cu/CEAs with the same mass concentration exhibit different absorption capacities for four kinds of solvents. Therefore, the effect of the oil/organic solvent types on absorption capacities of the Cu/CEAs is also further evaluated. Figure 7a shows the absorption capacities of functionalized cellulose aerogel with mass concentration of 0.8 wt % for various oils and organic solvents. As can be seen, the

0.8 wt % Cu/CEA presents very high absorption capacities, ranging from 67.8 to 164.5 g/g, specifically, the lowest absorption capacity for *n*-hexane and the highest absorption capacity for dichloromethane. Generally, the absorption capacities increase with the densities of the solvents. As shown in the Figure 7b, with the increase of the densities of oils and organic solvents, the absorption capacities are growing, presenting a relatively good linear relationship. The deviation could be due to the difference of volatility for different solvents.

The recyclability of absorbents is one of the key criteria for practical application of oil cleanup. The Cu/CEAs could be reused for absorbing oils/organic solvents through the distillation approach and the oils also can be recycled. Figure 8 shows the variation of absorption capacities of as-prepared

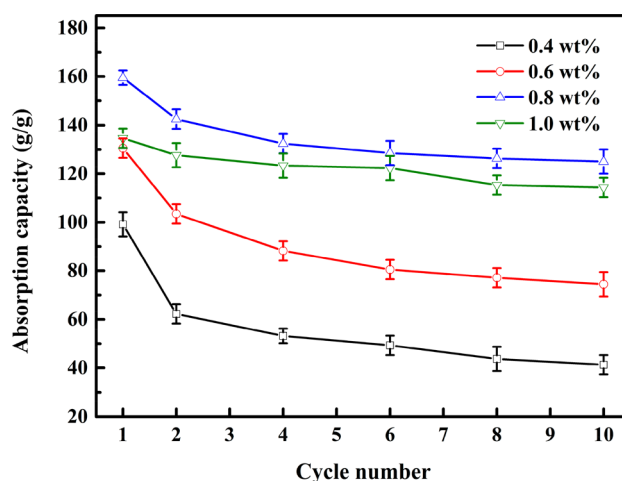


Figure 8. Variation of oil absorption capacity of CEAs with different mass concentration for trichloromethane with absorption cycle numbers.

Cu/CEAs with different mass concentration for trichloromethane during repeated absorption–release cycles. It can be seen that the absorption capacities of four kinds of Cu/CEAs all decreased to varying degrees with the increase of cycle times, among which the relatively obvious decrease of 0.4 and 0.6 wt % Cu/CEA, followed by 0.8 and 1.0 wt % Cu/CEA,

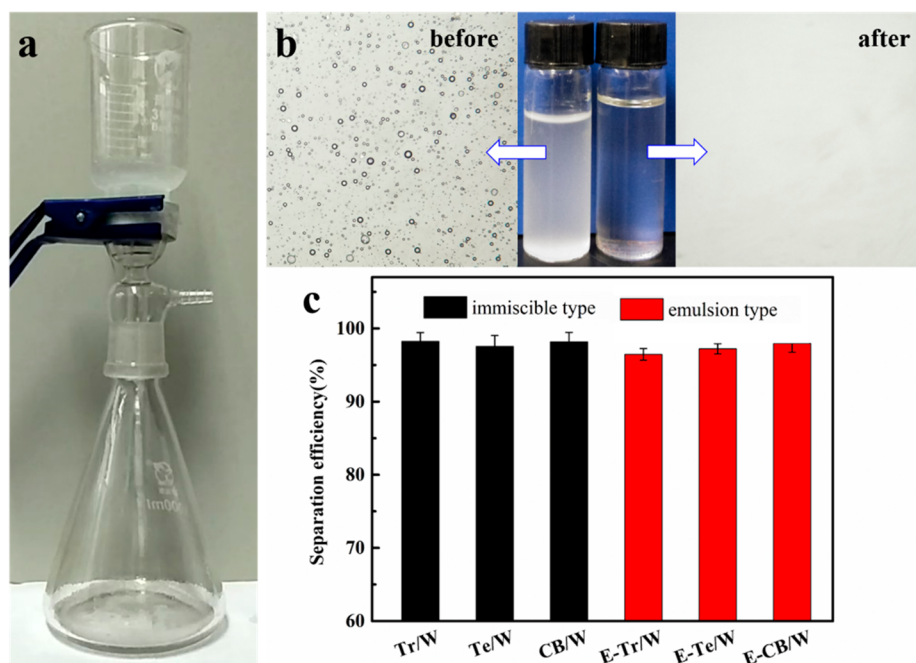


Figure 9. Digital photograph showing the process of emulsion separation under the gravity (a). Digital photos and optical microscopic images of emulsion before and after separation (b). Separation efficiencies of immiscible (including trichloromethane/water (Tr/W), tetrachloromethane/water (Te/W), and chlorobenzene/water (CB/W)) and emulsified (including E-Tr/W, E-Te/W, and E-CB/W) oil/water mixtures (c).

which indicate that the absorbency of Cu/CEAs is more stable with the increase of cellulose content. The difference of recyclability of Cu/CEAs with different mass concentration could be attributed to the effect of the mechanical properties of the aerogels themselves, which are also correspond to the analytical results from Figure S6. By comparison, 0.8 and 1.0 wt % Cu/CEAs possess better recyclability because of the strengthening effects of relatively high cellulose content. Moreover, from Figure 6a, the 0.8 wt % Cu/CEA has larger absorption capacity than that of 1.0 wt % Cu/CEA. Therefore, the Cu/CEA with the mass concentration of 0.8 wt % should be the most appropriate choice from the perspective of mechanical properties, absorption capacities, and recyclability.

Moreover, the as-prepared Cu/CEAs could act as a thick film to be used for efficiently separating oil/water mixtures including immiscible and emulsified types. When 50 mL of immiscible trichloromethane/water mixture (1/1, v/v) was poured into 0.8 wt % Cu/CEA with the height of 20 mm and the diameter of 35 mm, the oil was quickly absorbed, and the excess oil penetrated through the Cu/CEA and flowed into the flask beneath it in a short time (Video S3). Meanwhile, water was completely repelled and collected above the Cu/CEA. The whole separation process was achieved by only gravity without any external force, still showing a high flow rate. In the same manner, 50 mL of surfactant stabilized trichloromethane/water emulsion (1/49, v/v) was successfully and quickly separated under the driving of gravity (Figure 9a and Video S4), indicating the as-prepared Cu/CEA could be used to treat emulsions that are difficult to separate, significantly expanding the scope of application. The digital photographs and optical microscopic images of the trichloromethane based emulsion before and after separation are shown in Figure 9b. The trichloromethane based emulsion presents as milky with numerous micrometer water droplets, and the solution becomes transparent and no droplets could be observed after the separation. Figure 9c shows separation efficiencies of

various immiscible and emulsified oil/water mixtures. As can be seen, when the as-prepared Cu/CEA was used as membrane to separate oil/water mixtures, it presents high separation efficiencies of all up to 97% for immiscible and emulsified oil/water mixtures.

CONCLUSIONS

In summary, we have successfully fabricated superhydrophobic, flexible, and sustainable functionalized cellulose-based aerogel from low-cost natural sisal, Cu/CEA, through a simple approach. The superhydrophobicity of Cu/CEA was directly achieved by one-step depositing Cu nanoparticles on the surface of cellulose fibers via a facile redox reaction without any additional organic modification treatment, which is a more cost-effective and simple method of hydrophobization than previous reports. Moreover, this work has reported the effects of mass concentration (i.e., the cellulose content) on the performance of Cu/CEAs to determine the optimal value (0.8 wt %) after synthetical evaluation. The obtained highly porous Cu/CEA as absorbent exhibited high oil absorption capacity (67.8–164.5 g/g) and rate, and good recyclability. In addition, it can also act as a thick film to continuously and rapidly separate oil/water mixtures including emulsions and possesses very high separation efficiency (above 97%). Therefore, with the advantage of easy preparation and convenient use, the sustainable functionalized cellulose-based aerogel is expected to be an attractive candidate for large-scale cleanup of oil spills and purification of oily wastewater in versatile application.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b01122.

Absorption process and separation process for different types of oil/water mixtures: Cu/CEA was placed into the *n*-hexane/water mixture (AVI)

Absorption process and separation process for different types of oil/water mixtures: Cu/CEA can selectively absorb trichloromethane rather than water from the bottom of water in 7 s (AVI)

Absorption process and separation process for different types of oil/water mixtures: 50 mL of immiscible trichloromethane/water mixture (1/1, v/v) poured into 0.8 wt % Cu/CEA (AVI)

Absorption process and separation process for different types of oil/water mixtures: 50 mL of surfactant stabilized trichloromethane/water emulsion (1/49, v/v) was successfully and quickly separated under gravity (AVI)

Recycling process by adsorption–distillation approach; SEM images of functionalized cellulose aerogels with different mass concentration; WCA changes of functionalized cellulose aerogel at different conditions; the mechanical properties of functionalized cellulose aerogels with different mass concentration; the fitting results of absorption kinetics (PDF)

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Notes

The authors declare no competing financial interest.

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