

Preparation of magnetic hydrophobic polyvinyl alcohol (PVA)–cellulose nanofiber (CNF) aerogels as effective oil absorbents

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Abstract Efficient, rapid removal of oil spills on the surface of water is technologically significant for protecting the ecological marine environment. In this work, environmentally friendly, novel, magnetic hydrophobic PVA/CNF aerogels (MHPCA) with ultralow density (13.84 kg m^{-3}), high porosity ($> 98\%$), magnetic responsivity and good mechanical properties were successfully prepared by vacuum freeze-drying PVA/CNF gel followed by a facile silanization reaction and dipping process. The hydrophobic but oleophilic nature of the as-prepared MHPCA (water contact angle over 138°) came from the polysiloxane coated on the fiber surface by the silanization reaction. The MHPCA had excellent oil/water selectivity, with oil absorption capacity as high as 136 g/g being observed. Additionally, the MHPCA exhibited good magnetic response and could absorb oil on the surface of water by magnetic driving. More importantly, the MHPCA showed excellent elasticity after 30 compression-release cycles, which demonstrated the reusability and durability of the super absorbent. The results of this work provide a feasible idea for easily and efficiently removal of oil pollution from the water surface.

Keywords Cellulose nanofibers · Polyvinyl alcohol · Hydrophobic · Magnetic responsivity · Oil absorption capacity

Introduction

Because of the rapid development of the petroleum industry and the necessity of marine oil transportation, oil spill accidents have frequently occurred during oil transportation and oil mining. Oil spills not only have a negative impacts on the marine environment, but also threaten the surrounding ecological environment and human health (Shafir et al. 2007; Fingas 2012). Therefore, finding an effective way to resolve oil pollution is a pressing task for the entire international community. Currently, conventional methods used for dealing with oil pollution can be mainly divided into four groups: combustion methods (Liu et al. 2016), physical methods (Ge et al. 2014), chemical methods (Syed et al. 2011; Cho et al. 2014), and bioremediation (Prince 1997). Combustion methods cause waste of the crude oil. Considering physical methods, booms and skimmers are often used, but they are inefficient, especially when the proportion of oil in the oil/water mixture is low (Rajakovic et al. 2007). Dispersant and solidifying agent are often used in chemical methods to change the physical and chemical properties of oils. However, chemical methods are costly and harmful to the environment (Page et al. 2002). Bioremediation

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using microorganisms to degrade oils is environment-friendly and effective, but its efficiency is significantly affected by oxygen, temperature and pH (Prince 1997).

Compared with traditional methods, physical absorption has attracted considerable attention for cleaning up oil spills from the water surface due to its easy operation, high adsorption capacity and low cost (Wang et al. 2016; Zhou and Chuai 2010). To date, for the purpose of removing oily contaminants, various types of absorbent materials have been widely used in practical applications. These include inorganic sorbents (Karakasi and Moutsatsou 2010; Bastani et al. 2006), such as silicon dioxide, fly ash and organoclay, organic sorbents (Bayat et al. 2005; Choi and Cloud 1992), such as sawdust, peat, activated carbon and plant fibers and synthetic organic sorbents (Zhu et al. 2011; Lin et al. 2012; Wahi et al. 2013), such as polyvinyl polyurethane, polyvinyl chloride and polystyrene foam materials. However, shortcomings of these absorbent materials are also obvious. For example, the absorption capacity of inorganic sorbents and organic sorbents are poor. Additionally, these sorbents have the problem of absorbing not only oils but also water during the absorption process (Bastani et al. 2006; Nakazawa and Somorjai 1995). Although synthetic organic sorbents are highly hydrophobic, these sorbents may cause secondary pollution, and degradation remains a major environmental challenge (Lee et al. 2016). Therefore, it is necessary to identify better adsorption materials with high oil absorption capacity that are environmentally friendly, hydrophobic and oleophilic.

Cellulose-based aerogels showed potential in oil absorbents due to their large specific area and high porosity (Chin et al. 2014; Feng et al. 2015; Innerlohinger et al. 2006; Jin et al. 2015). Several efforts have been made to develop cellulose-based aerogels with high hydrophobicity by coating them with hydrophobic polymer or metallic oxide. For instance, cellulose-based aerogels were treated with methyltrimethoxysilane to obtain hydrophobic surfaces with a water contact angle over 153° (Feng et al. 2015). In another research, cellulose-based aerogels were coated with titanium dioxide (TiO_2) (Innerlohinger et al.) for oil removal from the water surface. C. D. Jin and S. J. Shen recently reported superhydrophobic and superoleophilic aerogels that were prepared from waste newspaper treated with

trimethylchlorosilane (Jin et al. 2015). These studies demonstrated that cellulose-based aerogels with hydrophobic modification have potential applications in the removal and recovery of pollutants from oil spills.

Although cellulose-based aerogels treated with hydrophobic modification from renewable cellulose fibers are desirable materials for oil spills, inherent inferior strength and modulus have limited their practical applications. PVA, as an excellent water solubility and biocompatibility filler, could enhance the mechanical properties of cellulose-based aerogels owing to the strong hydrogen bonding (Zheng et al. 2014). Besides, driving oil absorption materials to the polluted surface of water and collecting absorption materials rapidly after absorption also needs to be solved. Some researchers have proved that magnetic composite materials can solve this problem effectively (Wang et al. 2016; Raj and Joy 2015; Ge et al. 2013; Yu et al. 2017; Reddy et al. 2016; Chen et al. 2013; Gu et al. 2014). Therefore, we have sufficient reasons to believe that magnetic aerogel can be a promising candidate for oil pollution.

In this work, high selectivity, high oil absorption capacity and environmentally friendly magnetic CNF/PVA aerogels were developed using a facile freeze-drying process followed by hydrophobic modification and simply dipping into Fe_3O_4 nanoparticles solution. The aerogels had low densities (13.84 kg m^{-3}), high porosities ($> 98\%$) and good magnetic response. After treatment with methyltrichlorosilane (MTS) by a simple thermal chemical vapor deposition method, the aerogels showed excellent absorption abilities for several kinds of oils with hydrophobic characteristic. The aerogels could be easily collected from water surface by applying an external magnetic field after absorption. Furthermore, the aerogels exhibited excellent elasticity and high mechanical durability. The characterization of the aerogels were performed with scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD). The oil absorption capacity, relationship of oil absorption capacity to different time intervals (0, 5, 10, 15, 20, 30 and 60 s), magnetic removal process and reusability were also investigated in this paper, which described a potential material for the removal of oils from the water surface.

Experiments

Materials

All chemicals were of reagent grade and used without further purification. Analytical grade iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 25% ammonia solution, sulfuric acid (H_2SO_4), polyvinyl alcohol (PVA, MW:145,000 g mol^{-1}), glutaraldehyde (GA, cross-linker, 25 wt% in H_2O), anhydrous ethanol and methyltrichlorosilane (99 wt%) were purchased from Aldin. Bamboo powder was sieved by a 60-mesh filter and later vacuum-dried and set aside.

Preparation of cellulose nanofibers (CNFs)

The chemical purification of bamboo fibers were carried out based on the previous studies (Chen et al. 2011), and the CNFs slurry was mechanically lapped by a grinder (MKCA6-2, Masuko Sangyo Co., Ltd., Japan) at 1500 rpm (Abe and Yano 2010).

Preparation of Fe_3O_4 nanoparticles

In this study, Fe_3O_4 nanoparticles were synthesized by a chemical co-precipitation method according to previous report (Lin et al. 2016). Briefly, approximately 5.838 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 2.147 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were uniformly mixed in 100 ml deionized water. Next, the mixed solution was added into a three-necked flask with vigorous stirring at 60 °C under nitrogen. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25 wt%) was added to the solution and pH of the solution was controlled between 10 and 11. The temperature of the whole system was increased to 80 °C and sustained for 1 h. At the final stage, the resulting Fe_3O_4 nanoparticles were isolated from the solvent by an external magnetic field and washed many times with deionized water until they became neutral. The Fe_3O_4 powder was dried at room temperature.

Preparation of PVA/CNF aerogels (PCA)

To prepare PVA/CNF aerogels (M_w : 14,500 g mol^{-1}), 5.0 g PVA was dissolved in 100 ml deionized water and stirred for 8 h at 85 °C until the PVA completely dissolved. Then, 4 ml PVA solution (0.05 g ml^{-1}) and 30 g CNFs (0.67 wt%) were mixed together and stirred

for 1 h. The weight ratio of PVA and CNF was 1:1. Then, the crosslinking agent glutaraldehyde (200 μl , 25 wt%) and sulfuric acid (50 μl , 2.0 vol%) were added to the PVA/CNFs solution. The mixture was stirred for 1 h. Finally, the resulting mixture was placed in an ultrasonic bath for 10 min to remove any bubbles and subsequently crosslinked/cured in a vacuum oven at 75 °C for 3 h. The PVA/CNF aerogels were obtained using a freeze-drying process for 48 h at -60 °C.

Preparation of hydrophobic PVA/CNF aerogels (HPCA)

In this paper, chemical vapor deposition (CVD) technique was used for the surface modification of PVA/CNF aerogels. The obtained PCA was placed in a big glass bottle with a small open glass vial containing MTS (300 μl). The glass bottle was capped and heated in an oven at 60 °C for 8 h for the silanization reaction, then the modified aerogels were obtained.

Preparation of magnetic hydrophobic PVA/CNF aerogels (MHPCA)

Approximately 20 mg Fe_3O_4 nanoparticles were ultrasonically and dispersed in 20 ml ethanol solution. Next, the HPCA was dipped into the mixed solution for 30 min. The MHPCA was obtained using a freeze-drying process for 12 h at -60 °C.

Sample characterization

The density of PCA, HPCA and MHPCA were determined by measuring the volume and weight of each individual sample. The porosity of PCA, HPCA and MHPCA were calculated based on the following formula (1),

$$P(\%) = \left(1 - \frac{\rho}{\rho_s}\right) \times 100\% \quad (1)$$

where ρ was the density of the PCA, HPCA and MHPCA, respectively and ρ_s was the density of the solid material. Gemini analyzer (Micromeritics, USA) was used to test the Brunauer–Emmett–Teller (BET) specific surface area of PCA, HPCA and MHPCA. The BET of all samples were determined by analyzing the amount of N_2 adsorbed on the samples with the

relative vapor pressure (P/P_0) ranging from 0.0 to 1.0 at $-196\text{ }^\circ\text{C}$. The crystallinity of Fe_3O_4 was characterized by an X-ray diffraction instrument (D8-Advance, Bruker AXS diffractometer, German) with Cu-K α radiation ($\lambda = 1.54\text{ \AA}$, 40 kV, 30 mA, $2\theta = 10^\circ\text{--}70^\circ$), and the magnetic measurement was performed using a Quantum Design MPMS 7T SQUID VSM. The microscopic morphology of the samples were observed by a scanning electron microscope (FE-SEM, Hitachi S-4800). Functional groups of samples were observed by a Fourier transform infrared spectrometer (Nicolet iS10, Thermo Scientific Inc, USA). The surface wettability of PCA, HPCA and MHPCA were measured by water contact angle (WCA) (OCA40, Micro, Germany) at ambient temperature.

Oil absorption experiments

The oil absorption capacity of the MHPCA was determined based on the method reported in previous study (Zhou et al. 2016). All tests were performed at $25\text{ }^\circ\text{C}$. Briefly, the oil was poured on the surface of water in a beaker. Then, a piece of MHPCA ($\sim 50\text{ mg}$) was gently placed on the surface of the oil–water mixture. After entirely wetted by oils, the MHPCA with the absorbed oils were collected by sharp needle tweezers. The MHPCA was weighed after removal of excess oils using a filter paper. The oil absorbent capacity k of MHPCA was calculated according to formula (2),

$$k = \frac{m_2 - m_1}{m_1} (g/g) \quad (2)$$

where m_1 and m_2 are the weights of MHPCA before and after absorption, respectively.

In this study, we measured MHPCA oil absorption capacity for four different types of oil (soybean oil, corn germ oil, pump oil, used pump oil, gasoline, motor oil, ethanol and DMF). All tests were repeated three times, and the average capacity was reported. To investigate the oil absorption capacity of MHPCA, the aerogels were immersed in four types of oil (soybean oil, pump oil, motor oil and DMF), lifted from the oil, drained and weighed at different time intervals (0, 5, 10, 15, 20, 30 and 60 s). The compression strain rate was tested at 2 mm/min . The samples (with a diameter of 10 mm and height of 15 mm) were used for the test.

Results and discussion

Physical properties, crystallinity, magnetization and morphology

Table 1 summarizes the physical properties of PCA, HPCA and MHPCA. All of the samples had low densities ($< 14\text{ kg m}^{-3}$) and high porosities ($> 98\%$). Although the values of BET is very low, there was no great influence on the oil-absorption capacity of MHPCA. BET is usually used to test the micropores and mesopores of materials (Zhu et al. 2017), but the main pore structure of PCA, HPCA and MHPCA were macropores. Such pore structure can also provide similarly huge storage space and adsorption sites (Feng et al. 2015).

As shown in Fig. 1a, Fe_3O_4 nanoparticles had a spherical shape with rough surface, and the particle size of the Fe_3O_4 nanoparticles ranged between 20 and 30 nm. The crystalline structure of the magnetic Fe_3O_4 nanoparticles were characterized by an XRD pattern. The 2θ angles at 30.1° (2 2 0), 35.5° (3 1 1), 42.8° (4 0 0), 53.4° (4 2 2), 56.9° (5 1 1) and 62.3° (4 4 0) are typical diffraction peaks of Fe_3O_4 (Fig. 1b) (Anbarasu et al. 2015). Figure 1c summarizes the magnetic properties of Fe_3O_4 nanoparticles. The magnetization curve is a convincing proof (zero coercivity and magnetization increasing linearly at high fields) that the Fe_3O_4 nanoparticles have superparamagnetic properties. In order to make the HPCA show good magnetic response, Fe_3O_4 nanoparticles were added. From previous studies, superparamagnetic Fe_3O_4 nanoparticles would endow composite materials with good magnetic responsiveness (Wang et al. 2016; Chin et al. 2014; Raj and Joy 2015; Ge et al. 2013; Yu et al. 2017; Reddy et al. 2016; Chen et al. 2013; Gu et al. 2014). Figure 1d–f shows the microstructure of PCA, HPCA and MHPCA at the cross-section in the middle of the samples. All samples were highly porous and a three-dimensional (3D)

Table 1 Physical properties of PCA, HPCA and MHPCA

Sample	Density (kg m^{-3})	Porosity (%)	S_{BET} ($\text{m}^2\text{ g}^{-1}$)
PCA	11.48	99.01	13.24
HPCA	12.87	98.97	13.77
MHPCA	13.84	98.95	13.58

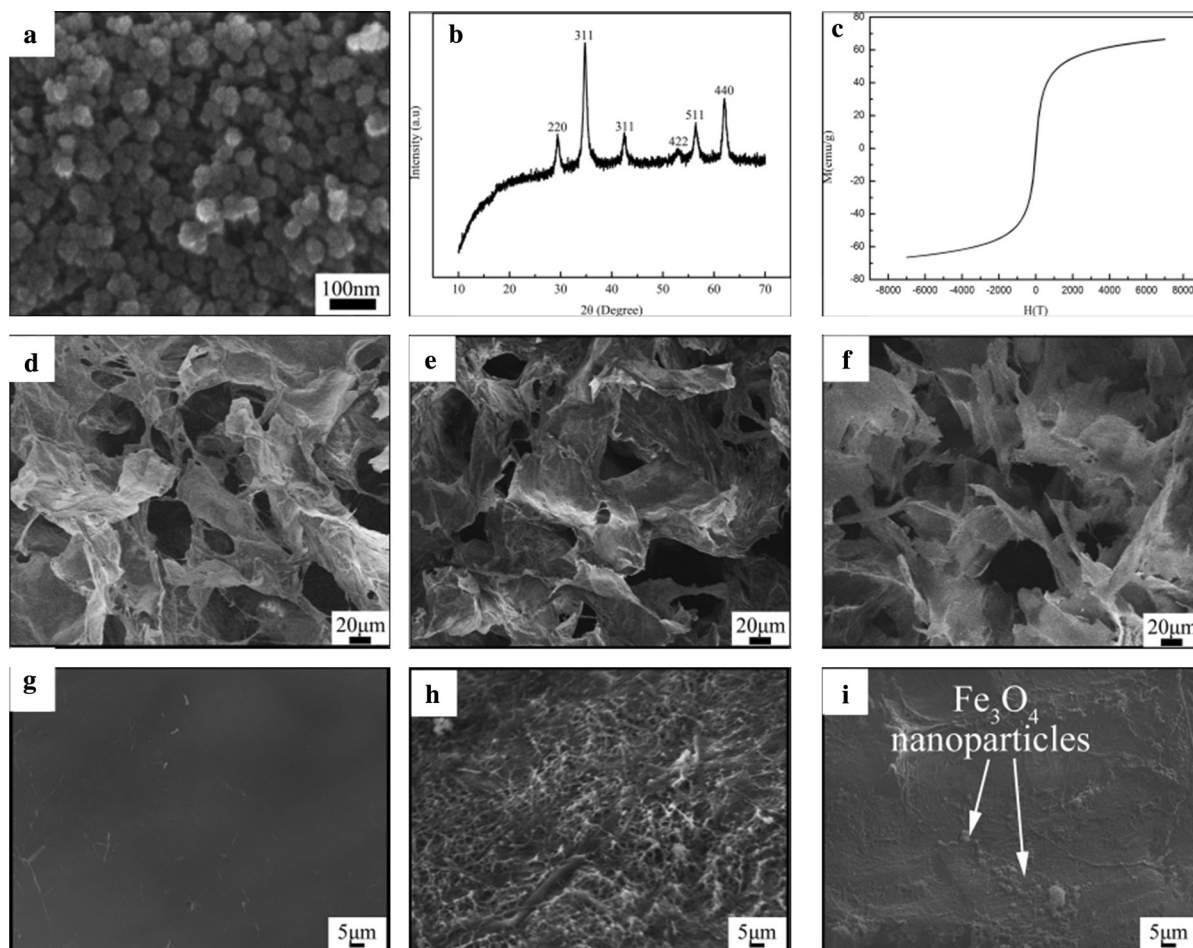


Fig. 1 **a** SEM image, **b** XRD and **c** Room temperature M versus H curves of Fe_3O_4 nanoparticles; **(d, g)**, **(e, h)** and **(f, i)** are the SEM images of PCA, HPCA and MHPCA, respectively

assembly of random nanofilaments by PVA and cellulose common structure that contributed the high liquid absorption capacities to the all aerogels. Actually, PVA and cellulose nanofibers were dispersed in water equably during the preparation of PVA/CNF hybrid mixture. After freeze-drying, both of them composed the sheet structure of aerogels owing to powerful hydrogen bond interaction between them (Han et al. 2016). The similar hole structure also illustrated that the MTS treatment and magnetization process had small effects on the primitive porous structure of PCA. However, there were differences in terms of what was observed on the PCA (Fig. 1g) cellular walls because numerous nanofiber-like structures were formed on the HPCA (Fig. 1h) and MHPCA (Fig. 1i), which was attributed to the formation of silicone nanofilaments (Artus et al. 2006;

Zhang and Seege 2011). Because of the unique load mode, the Fe_3O_4 nanoparticles distributed in the surface of sheet structure randomly and some of them have obvious reunification. It can be observed that the Fe_3O_4 nanoparticles were loaded onto the fiber surface in Fig. 1i.

FTIR spectrum

Successful hydrophobization on the porous surface and magnetization of PVA/CNF aerogels were further evaluated by FITR analysis (Fig. 2). Two absorption bands located at 780 and 1272 cm^{-1} were observed, which are ascribed to the characteristic vibrations of Si–O–Si and C–Si asymmetric stretching, respectively (Zhu et al. 2013). It was also observed that the spectra of MHPCA vibration intensity increased at 586 cm^{-1}

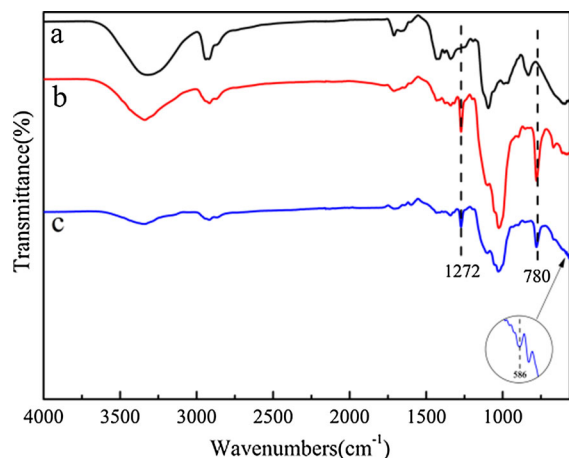


Fig. 2 FTIR spectrum of **a** PCA, **b** HPCA and **c** MHPCA

which may be caused by the characteristic peak of Fe_3O_4 around 586 cm^{-1} (Anbarasu et al. 2015). This observation further confirmed that magnetite nanoparticles are strongly anchored on aerogels.

Surface wettability

Water contact angles were measured to determine the surface wettability of PCA, HPCA and MHPCA. As shown in Fig. 3a, the unmodified PCA exhibited hydrophilicity as the aerogels could absorb water droplets on the aerogels surface immediately, and the water contact angle of PCA was 0° . However, the modified HPCA and MHPCA had hydrophobic properties which exhibit WCA up to 140° and 138° owing to the use of MTS (Fig. 3b, c). In previous reports, surface wettability was usually controlled by surface energy and surface roughness (Yang et al. 2015; Li et al. 2007). In this study, the silanization reaction caused decreased surface energy and high surface roughness by formation of polysiloxane particles during the silanization reaction process. The state of the water drops and dripping gasoline drops on the surface of the PCA, MPCA and MHPCA were also observed at the same time. It was observed that the PCA absorbed gasoline and water due to their amphiphilic properties (Fig. 3d). Conversely, the HPCA and MHPCA only absorbed gasoline, whereas water drops remained on the surface, revealing the selective absorption of oil/water (Fig. 3e, f). The tests

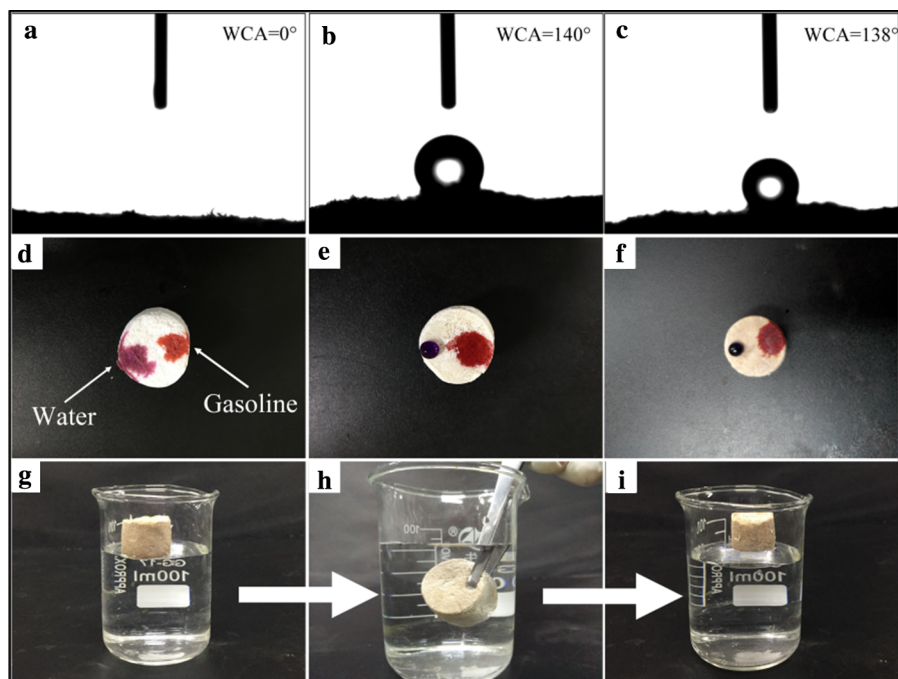


Fig. 3 **a–c** Water contact angle of PCA, HPCA and MHPCA. **d–f** Water (dye with KMnO_4) and gasoline (dye with Susan III) dropped on the surface of PCA, HPCA and MHPCA. **g–i** MHPCA before dipping, dipping and after dipping in water

also illustrated that the surface wettability of aerogel was only slightly changed by introducing Fe_3O_4 nanoparticles. To further confirm the hydrophobicity of MHPCA, aerogels were evaluated by dispersing the aerogels in water and measuring the internal surface wettability. The MHPCA was wrapped around by a layer of bubbles when immersed in water completely by an external force and floated on the water surface quickly after the external force was released (Fig. 3g–i).

Absorption capacity

To investigate the oil absorption capacity of MHPCA, a series of oils including soybean oil, corn germ oil, pump oil, used pump oil, gasoline, motor oil, ethanol and DMF, were tested and the results are shown in Fig. 4a. Absorption capacity (g/g) can be defined as the weight of the absorbed liquid per weight of original

MHPCA. The oil absorption capacity of MHPCA for all kinds of oils ranges from 59 to 136 times of its own weight, which is higher than other magnetic oil absorbing materials (Wang et al. 2016; Chin et al. 2014; Raj and Joy 2015; Ge et al. 2013; Reddy et al. 2016; Chen et al. 2013; Gu et al. 2014). Compared with other hydrophobic aerogels (Korhonen et al. 2011; Zhang et al. 2014; Wang et al. 2015; Feng et al. 2015; Jin et al. 2015; Yin et al. 2016; Zhou et al. 2016; Jiao et al. 2016; Zhu et al. 2017), MHPCA showed good performance for oil absorption as well as other advantage of magnetic responsivity. Different absorption capacity for oils was attributed to both surface properties of MHPCA and characteristics of oils, such as hydrophobicity, density and surface tension (Kim et al. 2012). The high organic solvent absorption capability exhibited by the MHPCA could be attributed to low density, developed pore structure, uniform hydrophobic and oleophilic silane coated on the fiber surface.

As shown in Fig. 4b, oil absorption capacity of MHPCA for soybean oil, pump oil, motor oil and DMF are plotted as a function of absorption time. The relationship between oil absorption capacity and absorption time can be divided into two stages: (1) a pure absorption stage and (2) a mixed absorption/desorption stage (Cheng et al. 2010). In the first stage, the oil absorption capacity increased rapidly, which can be explained by the high porosity of MHPCA. High porosity of aerogels provide a large number of fresh channels for oil particles so that they can enter the interior of the aerogel. Once the maximum absorption quantity of oil was achieved, the surface area of MHPCA was almost occupied fully by absorbed oils which prevented the aerogels from accessing free oil. In the second stage, the oil absorption capacity closed to equilibrium due to the oil absorption and oil desorption of oil molecules that happens concurrently. The maximum oil absorption capacity of MHPCA was achieved in less than 30 s for diesel oil, and the oil absorption capacity of MHPCA remained approximately the same as the removal time increased. These results demonstrated that MHPCA is of great potential for the rapid removal (Feng et al. 2015; Meng et al. 2015; Zhou et al. 2016) of oils from water surface.

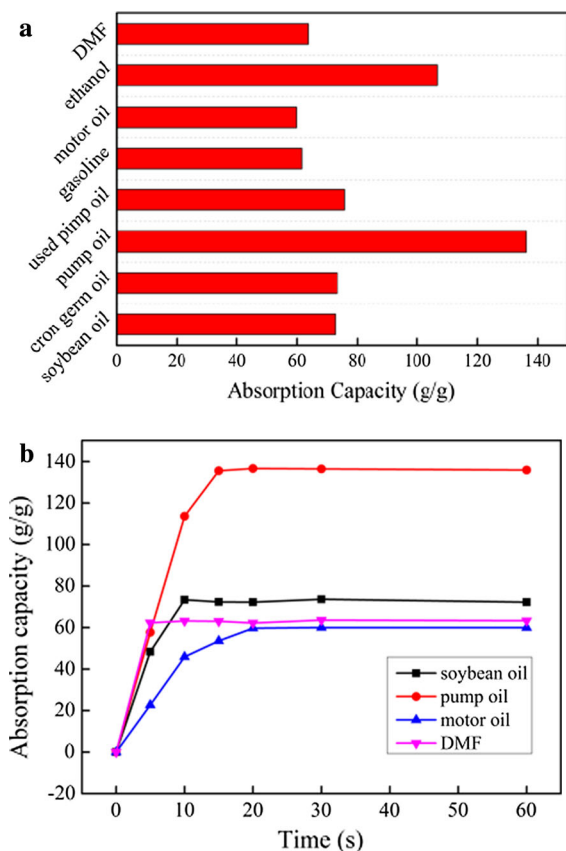


Fig. 4 **a** Oil absorption capacity of the MHPCA for various oils and organic solvents and **b** Oil absorption capacity of the MHPCA as a function of time

Effective oil absorption process

It is noted that magnetic property of MHPCA is very important and desirable for hassle-free treatment of polluted water. Figure 5a–f shows the effective absorption process (oil marked by Sudan III) using MHPCA under a magnetic field. Because of the silane treatment for aerogels, changes in chemical composition of aerogels surface endowed MHPCA hydrophobicity and lipophilicity (Cheng et al. 2017). It is predictable that MHPCA would absorb oils instead of water when exposed to oils floating on the water. The MHPCA also possessed some advantages like high porosity and unique 3-D interpenetrating network structure inherited from PCA. The high porosity gives huge storage space to MHPCA for oils and 3-D interpenetrating network structure provides fresh channels for oil particles to enter the interior of MHPCA easily (Liu and Chen 2014). Just as displayed by digital photographs, the MHPCA can be magnetically driven to the polluted region and quickly absorb oil while the sample repels the oil. After the absorption, the sample loaded with oil remained floated on the water surface while the water surface became completely clean. High selectivity, high oil absorption capacity, fast absorption rate and easy collection progress revealed the effective oil absorption of MHPCA.

Elasticity characterization and reusability

Figure 6a shows the height of recovery of MHPCA with good mechanical properties for which there is little decrease after 30 compression-release cycles. MHPCA showed excellent elasticity due to the toughness of PVA and the coated silane (Zheng et al. 2014). The cyclic compression stress–strain curves of MHPCA at a maximum strain of 70% were also shown in Fig. 6b. No obvious structural changes were found in the test and it showed excellent elastic recovery ability. The cyclic compression stress–strain curves demonstrate that MHPCA recovered almost back to their original shapes after 30 cycles, which show the good mechanical properties of MHPCA. Reusability is of great economic significance for oil absorption materials in oil clean-up applications. In this work, a simple absorption–extrusion–absorption method was used to test the reusability and durability of MHPCA. Figure 6c shows the cycle absorption process of MHPCA. After saturated with oil, most of the absorbed oils can be removed from MHPCA by mechanical squeezing easily. More interestingly, the squeezed sample can quickly absorb oil again and regain most of its volume.

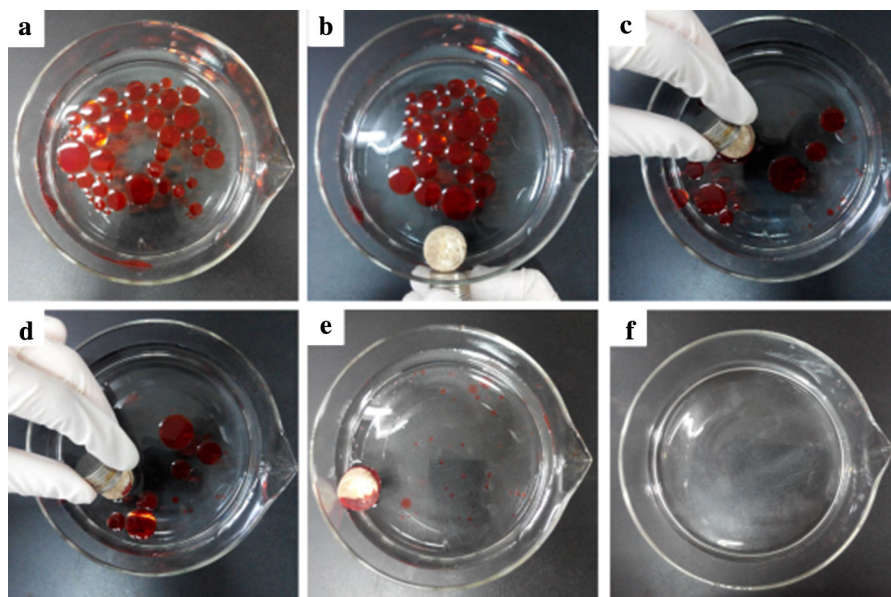


Fig. 5 Digital photographs (a–f) of removal of oil from the water surface by MHPCA and an external magnetic field

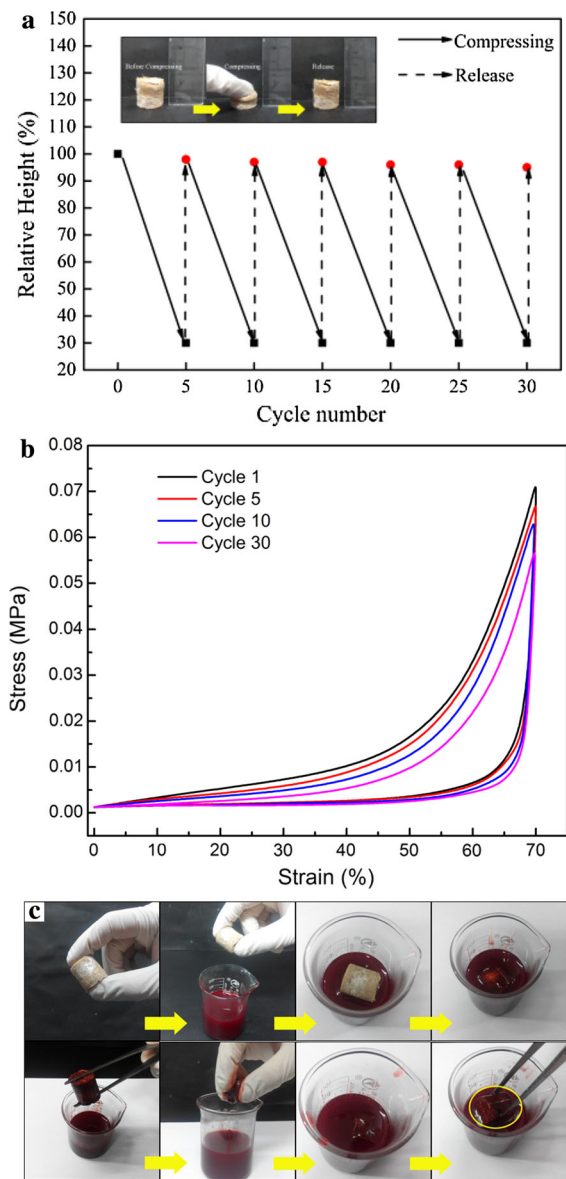


Fig. 6 **a** Height recovery of MHPCA as a function of cycle number at 70% compression strain. **b** Cyclic stress–strain curves of MHPCA subjected to a compressive strain of 70%. **c** Oil absorption reusability of the MHPCA

Conclusions

Hydrophobic and oleophilic magnetic PVA/CNF aerogels were successfully prepared by freeze-drying PVA/CNF gel followed by hydrophobic modification and a simple dipping method. The resulting aerogels have high oil absorption capacity for a series of oils (the maximum oil absorption capacity can reach

approximately 136 times of its original weight). Furthermore, good magnetic responsiveness drives MHPCA to the polluted region and is helpful for post-collection work. Thus, we have reasons to believe that this material has potential as an efficient and environmentally friendly oil absorbent for treating oil pollution in water.

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