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Facile Synthesis of Oil Adsorbent Carbon Microtubes by Pyrolysis of Plant Tissues

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ABSTRACT: Inspired by the nature of plant tissue, carbon nanomaterials such as nanofibers have been synthesized by pyrolysis of plant tissues. However, it is challenging in synthesis of tubular structure by pyrolysis because the structure is dynamical non-steady state and always collapse in carbonization process. Herein, carbon microtubes were synthesized by a simple carbonization method based kapok.

The tubular structure with the diameter ranges from 5-20 μm was obtained from the final carbon samples, which shows the similar structure with kapok precursors, while the weight was lost about 90%. We demonstrated that the carbon microtubes have excellent performance in oil adsorption with the adsorption capacity of $\sim 190 \text{ g g}^{-1}$, which is 1.5 times larger than that of raw kapok. We found that it is reusable for more than ten times in oil adsorption application, and the adsorption capacities of carbon microtubes significantly enhanced when the temperature increased in carbonization.

Keywords: Carbon nanomaterials; Carbon microtube; Oil adsorption; Kapok carbonization

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Introduction

Oil spill on ocean is hazardous and catastrophic for the marine environment and ecosystem. In recent years, the leakage and oil spills of tankers have been reported frequently [1]. For example, an explosion and fire occurs in the drilling rig Deepwater Horizon in 2010, and the fire blazed for 36 hours. This accident caused catastrophic damage to the drilling rig and marine ecological environment. A serious spill of diesel fuel up to 700, 000 US gallons (17, 000 bbl) was happened. Marine oil pollution caused by oil spill accidents in coastal areas not only brings huge economic losses, but also destroys marine ecological environment directly [2]. Recently, lots of efforts have been made to clear the floating oil, such as dispersion [3-4], burning [5], filtering by the membranes [6], and adsorption [7-10]. Among these methods, adsorption was the most efficient way because it is time saving and would not cause secondary pollution. Up to now, hydrophobic adsorption materials, including polyurethane foam [11-14], polydimethylsiloxane (PDMS) sponge [15-16], melamine sponge [17-18], carbon nanotube(CNT) sponges [19-21], carbon aerogels and foams [7, 22-24], have been synthesized and demonstrated the superior adsorption properties. However, these materials still have some limitations. For example, the expensive raw materials restricted them in real applications, and some of adsorption materials may cause secondary pollution. Therefore, it is still urgent to develop an ideal adsorbent materials, which should have high adsorption capacity and velocity, low density, environmental friendly, and reusable with cost effective properties.

Therefore, researchers devoted to develop oil sorbent materials from the natural

fibers, such as cotton, kapok, straw, populus seed [25-31]. Suni et al. [26] employed the cotton grass fibre as the sorbent for removing diesel oil, and the efficiency was over 99% with adsorption capacity of 20 g g^{-1} . Chen et al.[28] used the silica nanoparticles to hydrophobic modified coating on the surface of towel fabric and the oil absorption ratio increased to 9.75 g g^{-1} . Lv et al.[29] prepared silica particles modified cotton fiber by a sol-gel method and subsequent octadecyltrichlorosilane modification. Compared with raw cotton, the modified cotton absorbed different adsorption capacity of $25\text{-}75 \text{ g g}^{-1}$. Wang et al. [30] hydrothermal fabricated the ZnO nanoneedles on the surface of kapok fiber, and the result shows high adsorption capacities up to 70 g g^{-1} . Other agricultural products such as cotton [26], kapok [27], and populus seed [31], which is naturally hydrophobic have adsorption capacity of $40\text{-}60 \text{ g g}^{-1}$. Kapok has been widely used as an absorbing material. Nevertheless, the surface covered with waxy adds to the disadvantage of retaining oil on the fiber [32]. A few methods have been developed to enhance their adsorption properties. For example, the surface modification gives biomass materials improved adsorption capacity, stability and superhydrophobic [25, 32-34]. However, the procedure is complex and costly. Thermal treatment for pyrolysis is another way, which can enhance the porosity and the specific surface areas of these materials, and make them more oleophilic, as well as the water and volatile matter contents removal [35-37]. Previous reports have demonstrated that the thermal treatment of rice husks can lead to about twice higher adsorption capacity for the oil products than the raw materials [35]. As the husks do not have the hollow structure, the adsorption capacity is limited.

Tubular structure such as carbon nanotube and microtube owns a large specific surface areas, hollow structures, low density, hydrophobic and oleophilic and other properties, so it shows great potential in the application of oil adsorption. Currently, carbon based materials have been widely studied as adsorption materials for hydrogen and oxygen reduction reactions, but the investigation on oil adsorption is rare [36, 38-41].

In this study, inspired by microstructures of plant tissues, we synthesized carbon microtubes by carbonization of kapok fibers, and demonstrated their applications in oil adsorption. The as-prepared carbon microtubes have low density and porous structure characteristics, and performed a high adsorption capacity and efficiency in absorbing oils. The adsorption capacities were 110-190 g g⁻¹ for colseeds oil, olive oil and gasoline oil. These results provide a new avenue for synthesis of adsorption materials to clean the floating oil on the sea.

Materials and methods

Materials synthesis

The raw material is the kapok fiber obtained from the kapok trees in Yunnan Garden of Nanyang Technological University, Singapore. The pyrolysis of kapok was schematically illustrated in Fig. 1a. Firstly, 2~5 g kapok fibers were placed inside a quartz boat. Then the boat was set in the center of a tube furnace and filled into the flowing gas (N₂) about 500 sccm for 15 minutes to purge the tube, and maintained at 100 sccm during the whole process. The furnace was annealed at 500 °C, 800 °C or 1000 °C respectively at a rate of 5 °C/min and maintained 30 minutes under ambient

pressure. Finally, we stopped heating and cooled it naturally to room temperature.

Characterization

Scanning electron microscope (SEM, ProX Phenom) and transmission electron microscope (TEM, JEOL2100F) were used to determine the microstructure and morphology of the carbon microtubes. Raman spectroscopy of the carbon microtubes was collected by UHTS 300 VIS-NIR with the Ar laser excitation of 514 nm. The chemical structure of the kapok was characterized by X-ray photoelectron spectroscopy (XPS, PHI-5400). Thermal gravity analysis was used to investigate pyrolysis mechanism in carbonization process. Thermal gravimetric analyzer (TGA, Q600SDT) was conducted at the heating rate of 10 °C/min under the N₂ gas atmosphere. Static contact angle measurements were performed with deionized water and olive oil using a contact angle system OCA 15 Pro. The Brunauer-Emmett-Teller (BET) surface area was measured on a Micromeritics ASAP 2020 system at 77 K.

Oil adsorption tests

The adsorption capacity of carbon microtubes was measured by the oils including colseeds oil, olive oil, and gasoline oil. The mass adsorption capacities (Q) can be calculated as follow equation [20]:

$$Q = \frac{m_2 - m_1}{m_1} \quad (1)$$

where m_1 and m_2 represent the mass of carbon microtubes before and after oil absorption, respectively. The final mass adsorption capacity for carbon microtube materials were calculated by averaging the values from multiple measurements. To re-active carbon microtubes for multiple adsorption applications, the oil in the carbon

microtubes was removed and washed by hexane for three times. The materials were annealed in oven at 60 °C for 30 minutes to remove the residual hexane. After that, the carbon microtubes were ready for next adsorption. This process could be repeated several times for evaluation of the adsorption capacity and reusability of carbon materials.

Results and discussion

Figure 1b-e show the SEM images of original kapok and the carbon microtubes, which were thermal decomposed from kapok fibers at 500 °C, 800 °C, and 1000 °C, respectively. As shown in SEM images, the kapok fibers were thermal decomposed into carbon microtubes with similar microstructures and size. The average diameter is about 5-20 μm . The tubular structure of kapok fibers was not destroyed in carbonization process. After carbonization, the carbon microtubes display rough morphology, and obviously thinner than the kapok. SEM images (Fig. 1b-e) display that the diameter of kapok is 20 μm , and it was decreased to ~ 12 μm after carbonization at the temperature ranged from 500 °C to 1000 °C. Figure 1f displays the energy dispersive spectrometer (EDS) of original kapok fibers and carbon microtubes, which indicates a large number of oxygen doped into final carbon microtubes. From the side-view SEM image of carbon microtube (Fig. 1g), we can observe open-end tube with the irregular shape section due to the break under the strength. Thickness of the tube wall is around 200 nm. Figure 1h shows typical TEM and high resolution TEM (HRTEM) images of carbon microtubes, which indicate that the tube wall consists of amorphous carbon and crystalline carbon particles.

Figure 1 Synthesis and characterization of carbon microtubes. (a) Schematic illustration for synthesis of carbon microtubes by carbonization of kapok. SEM images of original kapok (b) and carbon microtubes carbonized at 500 °C (c), 800 °C (d) and 1000 °C (e), respectively. (f) Typical EDS of kapok fiber and carbon microtubes. (g) Cross section view SEM images and (h) TEM images of carbon microtube.

Figure 2a shows the thermogravimetry curves of the kapok. The weight dropped slightly from 20 °C to 65 °C for about 9% due to the loss of the moisture. Then the curves dropped sharply from 240 °C to 370°C for about 70%, indicating the major chemical reactions happen at this section. When the temperature increased from 500 °C to 1000 °C, 13 % weight of original materials was transferred to final carbon materials, and the value of weight is no longer changing, which suggests that no more reactions have occurred in this section. The TGA result suggests the carbonization

process occurred in the temperature of 240 °C-370 °C. Previous reports show that the high temperature favors the carbon materials to increase the porosity and the specific surface areas [42]. Hence, we have tried to increase the carbonization temperature to change the microstructure of the tubes to improve for increasing the adsorption performance. For understanding the chemical structures and crystallinity of the carbon microtube, the Raman spectra was used to identify the G-band and D-band of carbon materials. As shown in Fig. 2b, two peaks were obviously found around 1340 cm⁻¹ (D band) and 1595 cm⁻¹ (G band), which attribute to the defect of the carbon crystallite and the in-plane bond-stretching of C-C bonds, indicating the formation of the amorphous carbon in the fiber [43-44]. Figure 2c shows that the intensity ratio (I_D/I_G) of the D band and G band increased from 0.76 to 1.06 when improving the carbonized temperature from 500 to 1000°C, which suggests that structural defects of the carbon microtubes increased when the temperature increased [45]. The nitrogen adsorption and desorption isotherms is shown in Figure 2d with a BET surface area of 278.5 m²g⁻¹. The pore size distribution is calculated by using the Barrett-Joyner-Halenda (BJH) model according to the N₂ desorption isotherm part, as shown in Figure 2d (inset). There is a sharp peak centered at 2 nm and a broad band of 200~250 nm in the pore size distribution plot of the carbon microtubes, implying the existence of nano/micropores in the carbon microtubes.

Figure 2 (a) TGA curve of the kapok. (b) The Raman spectra of the kapok and carbon microtubes that carbonized at the temperature of 500 °C, 800 °C, 1000 °C, respectively. (c) The peak density ratio of D-band over G-band of samples carbonized at the different temperatures. (d) Nitrogen adsorption (blue circles), desorption (red circles) isotherm of the carbon microtubes that carbonized at the temperature of 1000 °C; inset shows the pore size distribution.

The XPS spectra of the kapok and the carbonized samples were used to identify the functional groups of the surface. The intact XPS spectra shows O and C elements. The detailed C1s spectra are shown in the Fig. 3. The C1s peaks of the samples can be resolved into two peaks, the peaks at 284.34eV are attributed to C=C/C-C, and the signal at 285.53eV represents the -C-O groups [46]. The result indicates the increase of the C=C/C-C bonds and the decrease of C-O bonds when the carbonize

temperature getting higher. Table 1 show the elements compositions of C and O with EDS analysis, the oxygen groups decreased with the increased temperature, the O takes only 6.5% when it was 1000 °C, indicating the dehydration, decarbonylation, and decarboxylation happened during the reaction [47]. As there is still O element exist after the carbonization, this may cause by the O element absorbed in the air and the incomplete carbonization.

Figure 3 XPS of kapok and carbon microtubes. Intact XPS spectra and related C1s spectra for the kapok (a, b) and the kapok carbonized at 500 °C (c-d), 800 °C (e-f) and 1000 °C (g-h), respectively.

Table 1 Atomic concentration of the kapok and carbonized samples

Samples	C1s	O1s

Kapok	67.8	32.2
500 °C	80.5	19.5
800 °C	85.6	14.4
1000 °C	93.6	6.5

The carbon microtubes were employed as oil adsorption materials for oil-water separation application because of the good hydrophobicity in their surface. We dropped the water and oil onto carbon microtubes respectively. The results show that the water droplets can stand well and kept globular shapes on surface of carbon microtubes, while the oil droplets were quickly spread and absorbed by this material (Fig. 4a). The contact angle measurements were performed to investigate the wettability of the carbon microtubes. The carbon microtubes showed a water contact angle of about 135° and the olive oil contact angle of about 37°, which indicated the hydrophobic surface of carbon microtubes. This result indicated the hydrophobic surface of carbon microtubes. To demonstrate its applications in oil adsorption, we exhibit images of the process of the carbon microtubes for cleaning the olive oil on the surface of the water. As shown in Fig. 4b-e, when the carbon microtubes were immersed in the mixture of the water and oil, the oil was absorbed within 5 seconds. When the carbon microtubes were pulled out from mixed solution, no color can be observed from the surface of the water, which indicated that the oil was fully removed from the water surface (Fig. 4e). The carbon microtubes show a good hydrophobicity and oleophilic properties, meanwhile, a high efficiency in absorbing oil.

The carbon microtubes also show a high adsorption capacity and good recyclability. In Fig. 4h, the column chart exhibited the adsorption capacity comparison between the kapok and carbon microtubes. The highest adsorption

capacity of carbon microtubes to colleseed oil, olive oil, and gasoline oil were established to be 182, 194 and 183 g g⁻¹ respectively. In addition, with the increasing of the carbonized temperature from 500 °C to 1000 °C, the adsorption capacity for gasoline oil significantly increased from 115 to 183 g g⁻¹. It is because the porosity and the specific surface areas increased in high temperature, which leads to the enhancement of the adsorption capacity. The highest capacity reached 181g g⁻¹ 194 g g⁻¹ and 183 g g⁻¹ for colleseed oil, olive oil, and gasoline oil. The adsorption capacities are higher than most of the sorbent, such as the dip-coated cotton and kapok (20-60 times) [48], superhydrophobic/superoleophilic corn straw fibers (15-23 times) [25], activated carbon-coated sponges (27-86 times) [16], and close to the recycled cellulose aerogels (40-95 times) [37], CNT sponge (92.3 times) [21], F-rGO aerogel (34-112 times) [24], while it is lower than the ultra-flyweight aerogels (215-913 times) [49]. The adsorption capacity is not only determined by density, viscosity and surface tension of the oils, but also by the packing density of the sorbent [50-51]. We believe a part of the oil was driven into the fibers through the pores with the capillary force and some adhere on the surface [52]. Before the carbonization, the oil is not easy to remain the fiber because the surface of the kapok was covered by the small amount of plant wax [53]. The experiment of repeated adsorption of colleseed oil was conducted for investigation of recycling properties of carbon microtubes. As shown in Fig. 4i, the adsorption capacity only decreased 20% of originals after 5 recycles, and the value can be kept to 70% after 10 cycles, which indicated a good recyclability. The high adsorption capacity and recycle properties make the material has great

potential applications in dealing with the floating oil on the sea.

Figure 4 Oil adsorption properties of carbon microtubes. (a) Water droplets stand on the surface of carbon microtubes, which indicates the hydrophobic surface properties of materials. (b-e) oil adsorption process by carbon microtubes (about 5 mg), where the 0.5 g olive oil was dropped to the water as the simulated floating oil. The carbon microtubes could achieve adsorption and separation of oils from water within 5s. (f-g) Photographs demonstrating the contact angle of carbon microtubes with a water (f) and (g) olive oil. (h) The summary of adsorption capacity of the kapok and its carbonized samples with various temperature. (i) Recycling and reusable performance of carbon microtubes in adsorption of olive oil.

Conclusions

In summary, we developed a simple method for synthesis of carbon microtubes. The method employed the plant tissue of kapok as precursors, making it easy to achieve large-scale fabrication. We demonstrated the oil adsorption properties of

carbon microtubes, and found the adsorption capacities of materials were related to the carbonization temperature of kapok. The adsorption capacity of the carbon microtubes can be established as high as 115-194 g g⁻¹ for the oils such as colseeds oil, olive oil, gasoline oil. The value can be significantly enhanced by increasing the carbonization temperature. The carbon microtubes show recycling performance in oil adsorption applications. The results show the carbon microtubes are promising absorbent for the treatment of floating oily contaminant in water.

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Conflicts of interest

The authors declare no competing financial interest.

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