

Preparation and Characterization of Carbon Microspheres From Waste Cotton Textiles By Hydrothermal Carbonization

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Abstract: Carbon microspheres were prepared from waste cotton fibers by hydrothermal carbonization (HTC) with the addition of copper sulphate in this work. The important influence factors, temperature, concentration of copper sulphate, resident time were explored here. The smooth and regular carbon microspheres could be formed at 330°C with 0.15 wt% copper sulphate after 6 h from waste cotton fibers. The crystal structures of cotton fibers were destructed in a short resident time with 0.15 wt% copper sulphate from SEM images and XRD patterns of solid products. This strategy provides a new, mild and efficient method to prepare carbon microspheres from waste cotton fibers by HTC. FTIR spectra verified that the abundant functional groups existed on the surface of synthesized carbon microspheres. From XPS and element analysis results, the copper sulphate participated in the forming process of carbon microspheres indeed. The presence of copper sulphate in the carbon microspheres provided a possibility for the application in antibacterial field. Besides, the catalytic mechanism of copper sulphate on the hydrolysis and carbonization of waste cotton fibers were also discussed. In conclusion, the copper sulphate is an efficient agent for preparing carbon microspheres by HTC from waste cotton fibers.

Keywords: Carbon microsphere; waste cotton fiber; copper sulphate; hydrothermal carbonization

1 Introduction

Recently, the waste textiles present an unprecedented upward trend, and the high output and the improper treatment of waste textiles brought on serious resource crisis and environmental problems. Specially, waste cotton fabrics have attracted growing attentions from researchers due to the high output and the high cellulose content of above 95%. Considering the high carbon content of 44%, it seems that the preparation of carbon materials from cotton textiles is a meaningful work. And it could solve the problem of the disposal and recycling of waste cotton textiles at the same time [1,2].

Waste cotton textiles, as a kind of cellulose materials, can be converted into carbon materials and energy using hydrothermal, chemical, biological processes and direct carbonization [3]. Commonly, the thermal process could produce activated carbon fiber, char, bio-oil, and syngas at high temperature [4-7]. Some research had produced improved surface area of activated carbon at a higher temperature, which would apply for various adsorbents allow for a wide spectrum of pollutants [7]. Moreover, carbonaceous materials from waste cotton fibers by carbonization have been investigated, including carbon nanofibers, carbon nanotubes, and porous carbons, which were used as the lithium-ion batteries anode materials [8-11]. And the carbonization temperature of cotton fibers was in range of 700-900°C, which has a larger energy input in this process than hydrothermal and chemical processes. However, the reported electrochemical performance is still limited by far.

Among of them, hydrothermal carbonization (HTC) had become the research center because of its mild

reaction conditions, simple operation, low cost, using water as solvent instead of organic solvent, high carbon yield, and more oxygen functional groups present the surface. Hydrothermal carbons have been proved to have very important applications in the preparation of porous carbon materials [12-14]. The first reported carbon spherules were synthesized by HTC of sucrose at 190°C through regulating the concentration of sucrose solution and reaction time in 2001 [15]. After that, more works were focused on the HTC of different saccharides at low temperature, including glucose, sucrose, starch and cellulose [13,16-21]. Meanwhile, the mechanism of hydrothermal and porous carbon products formation from different materials was also discussed with the characterization of XRD, FTIR, NMR and XPS [14,22-24].

So far, the materials for preparing carbon microspheres by HTC mainly focus on the glucose and microcrystalline cellulose, instead of the natural cotton fibers. The main reason is natural cotton fiber has a very complex HTC process due to its high crystallinity and degree of polymerization. And the past reports implied that the synthesis of carbon microspheres from cotton fiber is difficult by HTC. Therefore, various additives were used to improve the hydrolysis and carbonization of cellulose during HTC [25-27]. The methods of improving the conversion efficiency of cellulosic biomass during HTC could be classified into two aspects, promoting namely the hydrolysis rates of cellulose and the formation rates of carbonization products. For one thing, some works have been done to investigate the effect of the additives of H₂SO₄, HCl and acetic acid on the HTC of the cellulosic biomass [28], and as a result improved the hydrolysis efficiency of cotton fibers. The possible reason is cotton fibers are apt to hydrolyze to polysaccharide in concentrated acids since that the glycosidic bond is sensitive to a high concentration of H⁺ [24]. For another thing, the additives such as NH₄Cl, ZnCl₂, SnCl₂, CaCl₂ were also been studied to produce the highly porous carbon and increase the hydrothermal carbonization rates [26,27]. The results show that CaCl₂ could promote carbon nuclei to form hydrochar and influence the growth of carbon nucleus, when it is added in the hydrothermal process [26]. Similar reports indicate that the metal ion have an effect on the formation of carbon spheres during HTC of cellulosic biomass [29]. Therefore, the suitable additive is important to prepare carbon spheres from waste cotton fabrics at mild reactive condition during HTC.

In this work, different additives CuSO₄, Cu(NO₃)₂, CuCl₂, and MgSO₄ were introduced to the hydrothermal carbonization of cotton fibers to examine the formation of carbon microspheres. The optimal hydrothermal carbonization conditions with the addition of CuSO₄ were investigated, including the temperature, CuSO₄ concentration and resident time. Besides, the carbonized products were characterized with SEM, XRD, FTIR and XPS. Afterwards, the mechanism of hydrothermal carbonization was also explored with the addition of CuSO₄.

2 Experimental Methods

2.1 Materials

Waste cotton fabrics were obtained from Shanxi Greenland Textile Co. Ltd. All the chemicals were of analytical grade and purchased from Tianjin Guangfu Chemical Reagent Co., Ltd. The high-temperature autoclave (1L capacity with a maximum operating pressure and temperature of 42 MPa and 500°C respectively, and equipped with a feeding valve) was purchased from Run Chang Dalian Petrochemical Equipment Co., Ltd.

2.2 Hydrothermal Carbonization of Waste Cotton Fibers

All HTC experiments were carried out using the high-temperature autoclave. In a typical run, 12 g of cotton fibers was added in the 600 ml of deionized water and then placed into the reactor. After hydrothermal carbonization, the precipitate was collected by centrifugation (5000 rpm, 15 min) and then washed repeatedly with distilled water. Afterwards, the obtained solid was dried under a drying oven at 120°C for 12 h.

According to the designed experiments, the hydrothermal carbonization system was added with various additives (CuSO₄, Cu(NO₃)₂, CuCl₂ and MgSO₄), and was run at corresponding additive

concentration, reaction temperature and time.

2.3 Characterization of Carbon Microspheres

The morphologies of carbonization products were observed by field emission scanning electron microscopy (JSM-6700F, Japan-Electronics Company). The changes in crystal structures of samples were characterized by X-ray diffraction using a Y-2000 (Dandong Tong Da Technology Co., China). The functional groups of carbon spheres were measured by FT-IR spectroscopy using a Tensor 27 spectrometer (Bruker) with resolution of 4 cm^{-1} . To measure the elemental composition and chemical state of the surface elements (mainly C, O and Cu atoms) in the carbon spheres, XPS analysis was carried out with a VG Multilab 2000 X spectrometer. Elemental analysis (C, H, S and O) of the samples was performed on a Vario EL cube elemental analyzer (Elementar, Germany), the element of Cu of samples was analyzed on a Thermo iCAP 6300 inductively coupled plasma atomic emission spectrometer (Thermo Fisher, America).

3 Results and Discussion

3.1 Hydrothermal Carbonization of Cotton Fibers with Different Additives

Hydrothermal carbonization of cotton fibers was studied with the addition of metal-salts CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, CuCl_2 and MgSO_4 under the same HTC conditions. As shown in Fig. 1, the morphology of carbonized products of cotton fibers at 330°C after 8 h were displayed with CuSO_4 , $\text{Cu}(\text{NO}_3)_2$, CuCl_2 and MgSO_4 and without additive. For all samples, the structures of cotton fibers had a serious destruction after 8 h, but there was an obvious difference in carbonization extent and products morphology with the different additives. Notably, with the addition of CuSO_4 , the structures of cotton fibers were destructed completely, and the smooth and regular carbon microspheres were formed (Fig. 1(d)). In comparison, solid residue with $\text{Cu}(\text{NO}_3)_2$ remained a portion of fibrous structures and showed a slight carbonization (Fig. 1(b)). With CuCl_2 and MgSO_4 , the carbonized products presented in an irregular fragmental block structure (Fig. 1(c) and Fig. 1(e)). The SEM results indicated that the presence of CuSO_4 significantly promoted the formation of carbon microspheres, while the addition of other metal-salts had not a positive effect on the carbon microspheres preparation from cotton fiber by HTC. Moreover, the crystalline structures of cotton fibers were destructed totally after 8 h HTC from the XRD and FTIR results (Fig. S1). It was concluded that the hydrolysis and carbonization extents of cotton fibers had an obvious difference with the addition of different metal-salts in the HTC systems. The metal-salt CuSO_4 would have a positive effect on the formation of carbon microspheres from cotton fibers.

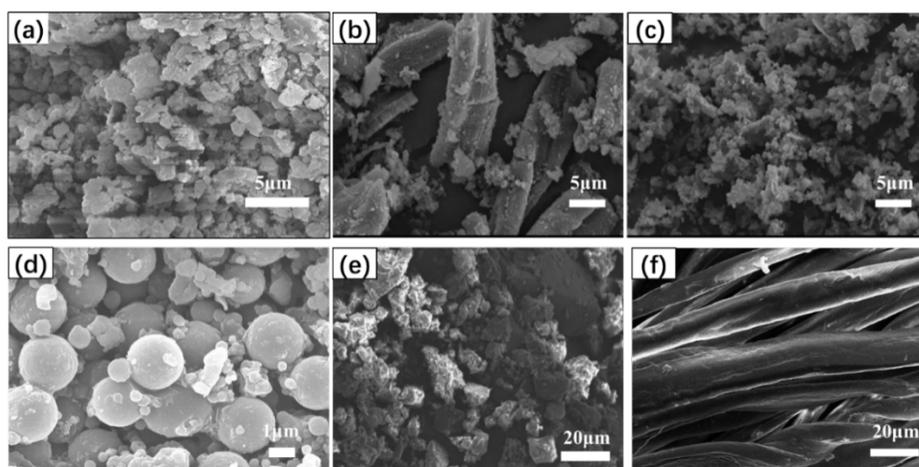


Figure 1: SEM images of carbonized products of cotton fibers with different additives at 330°C after 8 h HTC (a) without any additive (b) 0.15 wt% $\text{Cu}(\text{NO}_3)_2$ (c) 0.15 wt% CuCl_2 (d) 0.15 wt% CuSO_4 (e) 0.15 wt% MgSO_4 (f) raw cotton fibers

3.2 The Preparation of Carbon Microspheres from Cotton Fibers with CuSO_4

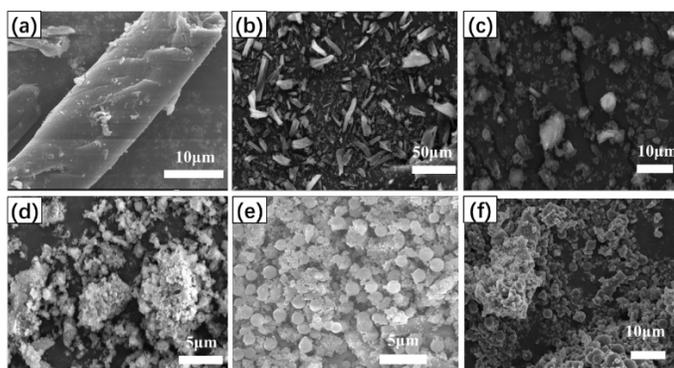
To obtain the optimal carbon microspheres from cotton fibers by HTC with CuSO_4 , the important factors of HTC (temperature, residence time and CuSO_4 concentration) were examined during the carbonization process of cotton fibers. Without any additive, the morphology and structure of cotton fibers after 8 h HTC was destroyed gradually with the increase of temperature in the range of 210°C to 330°C, but the carbonized products could not form the globular structures all the time (Figs. 2(a)-2(c)), which is in accordance with the previous reports [24,30].

3.2.1 Effect of HTC Temperature on Carbon Microspheres

The morphologies of carbonization products of cotton fibers in range of 210°C to 350°C were shown in Figs. 2(d)-2(f) and Fig. S2, with the addition of 0.15 wt% CuSO_4 concentration for 8 h residence time. In temperature range of 270-330°C, the uniform and regular carbon microspheres were synthesized, and the optimum HTC temperature was 330°C for the preparation of carbon microspheres. At either low or high HTC temperature, the presented carbon spheres had been unsatisfying. At a lower temperature of 210-270°C, a large amount of carbonized product appeared in the fragment state rather than spherical structures. At a higher temperature of 350°C, the carbonized products had a serious adhesion among carbon microspheres. Above results suggested that HTC temperature was important for carbon microspheres morphologies. Therefore, the optimum temperature was 330°C for the preparation of carbon microspheres from cotton fibers by HTC with CuSO_4 as additive.

The changes in crystalline structure of carbonized products were also examined during HTC processes of cotton fibers (Fig. 2(g)). Without CuSO_4 , the carbonized product remained the crystal structures of cotton fibers at 210°C after 8 h, and the crystal structure of solid products was destructed as the temperature rose to 240°C. The results agreed with the SEM results (Figs. 2(a)-2(b)). With 0.15 wt% CuSO_4 , the similar XRD patterns were observed for the solid products at 210°C, 240°C, 270°C and 330°C, which indicated that the crystal structures of solid products had been destructed completely. In comparison, the cotton fibers were hydrolyzed and carbonized at a lower temperature in the presence of CuSO_4 . That is to say, the addition of CuSO_4 in HTC system promoted the hydrolysis of cotton fibers.

Fig. 2(h) presented the changes in the yield of carbonized products in the range of 220°C to 330°C with and without CuSO_4 . In the range of 240°C to 330°C, the changes in carbonized products yield with temperature showed similar trend with and without CuSO_4 . Without the addition of CuSO_4 , a very high carbonized products yield was observed at the low HTC temperature of 220°C, which could be explained as the unhydrolyzed cotton fibers in the residues. From Fig. 2(h), the initial carbonization temperature was 240°C without CuSO_4 , while it decreased to 210°C with 0.15 wt% CuSO_4 , which indicated that it had a significant decrease in the initial carbonization temperature in the presence of CuSO_4 (0.15 wt%). In conclusion, the addition of CuSO_4 in HTC system has a positive effect on the hydrolysis and carbonization of cotton fibers, and it could decrease the initial temperature of HTC.



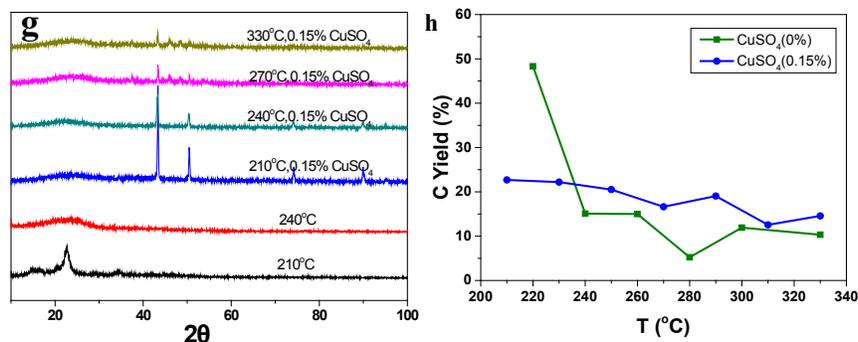


Figure 2: SEM images (a-f) and XRD patterns (g) of carbonized products of cotton fibers after 8 h at different temperatures with and without CuSO₄ (h) the changes curves of carbonized products yield after 8h in range of 210°C to 330°C with and without CuSO₄. (a) 210°C (b) 240°C (c) 330°C (d) 210°C, 0.15 wt% CuSO₄ (e) 330°C, 0.15 wt% CuSO₄ (f) 350°C, 0.15 wt% CuSO₄

3.2.2 Effect of CuSO₄ Concentration on Carbon Microspheres

Fig. 3 shows SEM images of carbonized products for HTC of cotton fibers in the range of 0.05 wt% to 0.25 wt% CuSO₄ concentrations at 330°C after 8 h residence time. It was obvious that the optimal carbon microspheres morphology and amounts were presented with the addition of 0.15 wt% CuSO₄ (Fig. 3(d)). We could find that the amounts of carbon microspheres presented an obvious increase trend as CuSO₄ concentrations increased from 0.05 wt% to 0.15 wt%, while the adhesion phenomenon among carbon microspheres was too serious to remain the spherical structures at a higher CuSO₄ concentration of 0.25 wt% (Fig. 3(e)). And there was almost noncarbon microsphere to form at a very low CuSO₄ concentration of 0.05 wt% under the same HTC condition (Fig. 3(a)). Therefore, the optimal CuSO₄ concentration of 0.15 wt% was used in the subsequent experiments for the preparation of carbon microspheres from cotton fibers by HTC with CuSO₄ as catalyst.

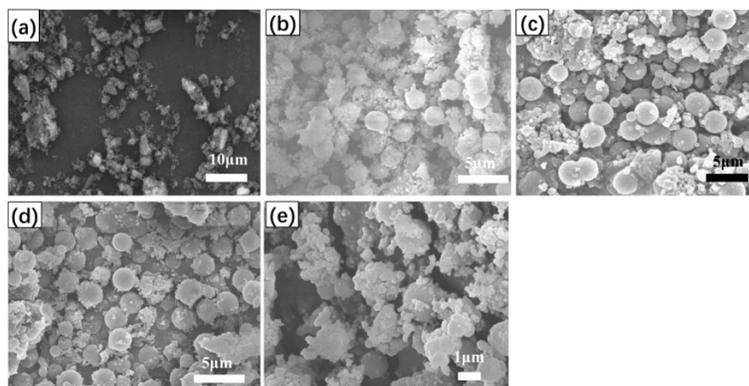


Figure 3: SEM images of carbonized products of cotton fibers at 330°C after 8 h with different CuSO₄ concentration (a) 0.05wt% (b) 0.1wt% (c) 0.15 wt% (d) 0.2 wt% (e) 0.25 wt%

3.2.3 Effect of Resident Time on Carbon Microspheres

Figs. 4(a)-4(e) displayed the changes of carbon microspheres morphology for resident time of 2 h to 10 h at 330°C with 0.15 wt% CuSO₄. At the initial stage of 2 h and 4 h resident time, carbonized products were mainly amorphous solid particles, but a small amount of solid began to gather into carbon microspheres and had an increase trend with the increasing of resident time (Figs. 4(a) and 4(b)). When the resident time prolonged to 6 h, many smooth and uniform carbon microspheres were synthesized, showing affine carbon microspheres formation situation. With the resident time further increased to 8 h and 10 h, the carbon microspheres sizes had a significant increase and the serious adhesion phenomenon

among carbon microspheres began to appear, thus the previous formed spherical structure was gradually collapsed. Fig. 4(f) showed the crystalline structure changes of cotton fibers after 2 h, 4 h, 6 h, 8 h and 10 h HTC. From Fig. 4(f), the similar XRD patterns were observed for all samples. And the broad diffraction peak appears for the products at $2\theta = 22.7^\circ$ (Crystal face index 002), which could be attributed to the diffraction peak of graphitic carbon. The large d_{002} suggested that the structure be highly disordered and the degree of graphitization be very low [31].

The possible reason was a low cotton fiber hydrolysis rate at the initial reaction stage, leading to a low glucose or oligosaccharide concentration and a low carbonized products yield at a short resident time [32]. When the concentration of monosaccharides or oligosaccharides increased to a certain value with the extension of resident time in HTC systems, the yield of carbonization products would have a dramatic rise, which provided a necessary condition for the formation of carbonization microspheres. However, a higher compounds concentration would cause a wide carbon microspheres size, thus the adhesion among carbon spheres made it difficult to remain the spherical structures. Above results indicated that the optimal carbon microspheres were synthesized after 6 h HTC at 330°C with 0.15 wt% CuSO_4 .

Fig. 4(g) shows that the effect of resident time on the carbonized products yields of cotton fibers at 330°C with 0.15 wt% CuSO_4 . In the initial phase of 2 h to 6 h, the yield of carbonized products increased slowly with resident time. Afterwards, it presented a rapid increase in carbonized product yield which was attributed to the accumulation of oligosaccharides in the earlier stage. Whereas there was an obvious decrease in carbonized products yields when the resident time prolonged to 10 h, due to the decomposition of carbon microspheres at high temperature.

It is concluded that during HTC of cotton fibers the resident time have an important effect on the controlling of carbon microspheres morphology and yield, but it has little impact on the crystal structure of carbonized products. Therefore, the optimal resident time of 6 h was selected for the preparation of carbon microspheres from cotton fibers by HTC with CuSO_4 as catalyst.

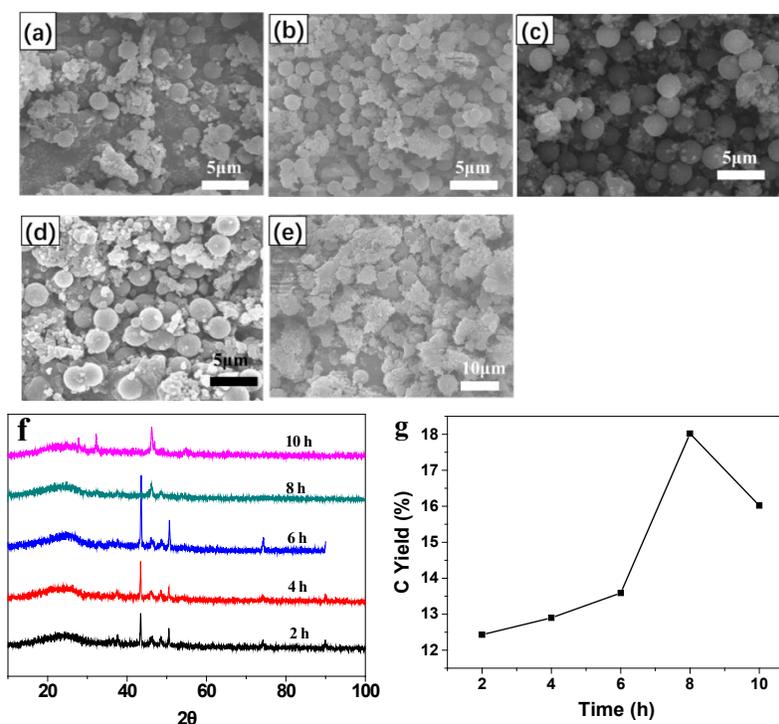


Figure 4: SEM images (a-e) and XRD patterns (f) of carbonized products of cotton fibers with 0.15 wt% CuSO_4 at 330°C at different resident time (a) 2 h (b) 4 h (c) 6 h (d) 8 h (e) 10 h (g) the change curves of carbonized products yield with the increase of resident time with 0.15 wt% CuSO_4 at 330°C

3.3 Characterization of Carbon Microspheres by HTC

The FTIR spectra of cotton fibers and carbon microspheres with CuSO_4 as catalyst are shown in Fig. 5. For samples, the broad band observed at 3000-3700 and 2900 cm^{-1} belongs to O-H (hydroxyl or carboxyl groups) and aliphatic C-H stretching vibration, respectively. The bands at 1710 and 1620 cm^{-1} (together with the band at 1513 cm^{-1}) can be attributed to C=O (carbonyl, quinone, ester, or carboxyl) and C=C vibrations, respectively, and the bands in the 1000 to 1450 cm^{-1} region correspond to the C-O (hydroxyl, ester, and ether) stretching vibration and O-H bending vibration. All these results suggested that surface functional groups of carbon microspheres became more abundant. Compared with the FTIR spectra of cotton fibers sample, the spectrum of carbonized products occurred the blue-shift, indicating the cotton fibers have been converted into carbon microspheres after 2 h HTC with the addition of 0.15 wt% CuSO_4 . The appearance of the bands at 1620 and 1513 cm^{-1} reveals the aromatization of the samples.

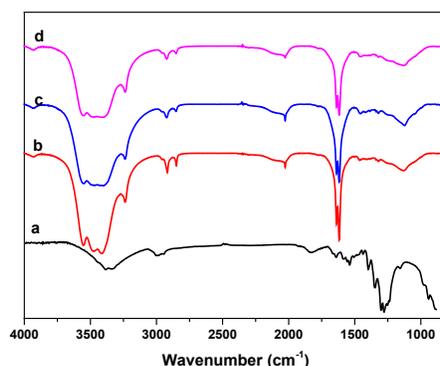
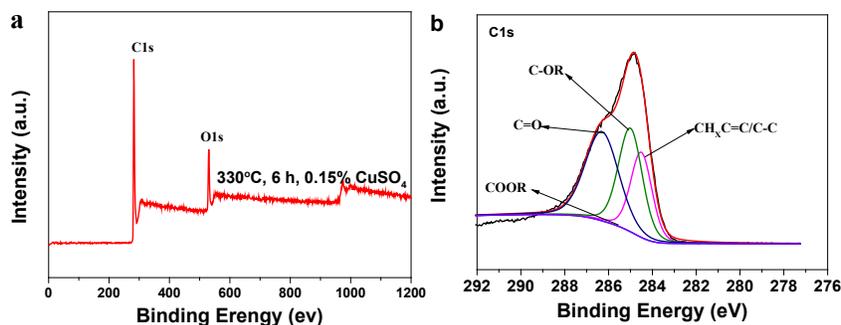


Figure 5: FTIR spectra of cotton fibers and carbonized products at 330°C with 0.15 wt% CuSO_4 under different conditions (a) cotton fibers (b) 2 h (c) 6 h (d) 10 h

Fig. 6 shows that XPS spectrum of carbonized products of cotton fibers with CuSO_4 as catalysis. From Fig. 6(a), the surface of carbon microspheres contained only the elements of C and O. The element of Cu does not exist in the surface of carbon microspheres or the contents of Cu element is too low to detect. But the results of elemental composition analysis proved that the content of Cu in the carbon microspheres was 12.52% with 0.15 wt% CuSO_4 at 330°C after 6 h (Tab. 1). The results indicated that CuSO_4 in the HTC system did participate in the synthesis process of carbon microspheres. The surface functional groups of carbon microspheres were analyzed via the peak splitting diagrams of C1s and O1s (Fig. 6(b) and Fig. 6(c)). As shown in Fig. 6(b), the functional groups of CHX (C=C and C-C) in benzyl structure were matched with the peak at 284.5 eV, and the functional groups of C-OR (C-OH and C-O-C), C=O, and COOR were characterized by the peaks at 285.0 eV, 286.3 eV and 288.7 eV. In Fig. 6(c), the peaks at 531.6 eV, 532.8 eV and 534.0 eV represented the functional groups of C=O, C-OH and C-O-C, respectively. The results of XPS spectra analysis further proved the results of FTIR analysis. Therefore, it is deemed that the additive of CuSO_4 mainly took part in the formation of crystal nucleus and promoted the synthesis of carbon microspheres from cotton fibers by HTC.



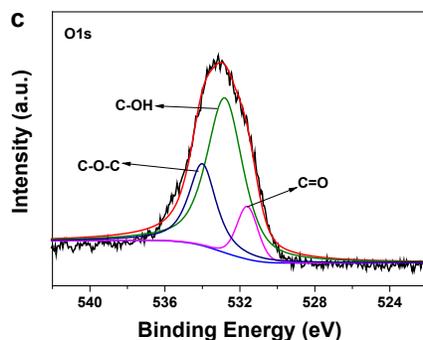


Figure 6: (a) XPS spectrum of the carbon microspheres after HTC. (b) and (c) display the corresponding C1s and O1s peaks of carbon microspheres with 0.15 wt% CuSO₄ after 6 h at 330°C

The H/C atomic ratios could provide information on the aromatic contents in solid products [12]. For the solid products at 330°C after 8 h, the higher H/C ratio of 0.76 was shown than that of 0.62 at 330°C after 4 h with 0.15 wt% CuSO₄. The higher H/C ratio indicated that the lower degree of aromatization in carbon microspheres was occurred for a shorter resident time in the presence of CuSO₄. That is, the addition of CuSO₄ in HTC system promoted the carbonization of cotton fibers. Besides, the value of H/C implied that the carbonization extent increased with the increase of HTC temperature and the prolong of retention time.

Table 1: Elemental composition (wt%) of carbonized products of cotton fibers at different carbonization condition

HTC conditions	C (%)	H (%)	S (%)	O (%)	Cu (%)	H/C
330°C -8 h	75.95	4.825	-	18.12	-	0.76
250°C-8 h-0.15% CuSO ₄	64.04	3.57	0.38	17.84	-	0.67
290°C-8 h-0.15% CuSO ₄	66.16	3.57	0.47	16.27	-	0.65
310°C-8 h-0.15% CuSO ₄	63.41	3.33	1.95	15.78	-	0.63
330°C-8 h-0.15% CuSO ₄	67.04	3.14	1.63	13.90	-	0.56
330°C-4 h-0.15% CuSO ₄	64.31	3.34	2.56	16.71	-	0.62
330°C-6 h-0.15% CuSO ₄	66.01	3.30	1.72	15.04	12.52	0.60

3.4 Catalytic Mechanism of CuSO₄ on the Formation of Carbon Microspheres from Cotton Fibers

Above results suggested that cotton fibers could be carbonized to form carbon microspheres by HTC with the addition of CuSO₄. The morphologies of carbon microspheres were closely related to temperature, resident time and CuSO₄ concentration in HTC system. As we all know that the HTC of cotton fibers underwent the cellulose hydrolysis and hydrothermal carbonization of polysaccharides [21,25]. In this study, the positive effect of CuSO₄ on the formation of carbon microspheres embodied the accelerating hydrolysis rates and carbonization rates. The possible mechanism of cotton fibers was shown in Fig. 7. In the first step, the additive CuSO₄ catalyzed hydrolysis of cellulose produced oligosaccharides, monomers (glucose and fructose) and other by-products [28]. Then the polymerization of monomers was built up by intermolecular dehydration, leading to the formation of soluble polymers. And the carbon nucleus was formed as the concentration of these polymers was critical to the nucleation. When additive CuSO₄ was added in the hydrothermal process, it could promote carbon nuclei to form and influence the growth of carbon nucleus. The similar results have also been reported in the references [26]. Besides, the results of elements analysis have verified that the additive CuSO₄ indeed participated the formation process of carbon microspheres.

As we all know that carbon spheres by HTC have been applied in the areas of adsorption, energy storage, catalyst support [33-35]. In this work, the addition of Cu in the carbon microspheres would provide a possibility for application in the antibacterial field. Further work would be done to explore the antibacterial property.

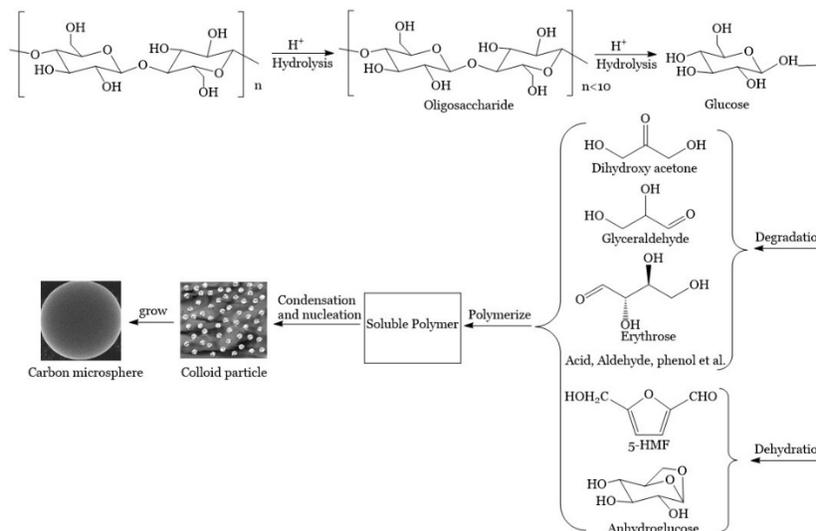


Figure 7: Mechanism of carbon microspheres from cellulosic materials by HTC

4 Conclusions

In this study, carbon microspheres could be synthesized from waste cotton fiber by HTC with the addition of CuSO_4 . And the smooth and regular carbon microspheres were obtained at 330°C after 6 h resident time with 0.15 wt% CuSO_4 . In the presence of CuSO_4 , the initial carbonization temperature fell from 240°C to 210°C , and the crystal structures of cotton fibers were destructed in a short resident time. A large amount of functional group on the surface of carbon microspheres were found from FTIR and XPS spectrum. Based on the above results, it is inferred that CuSO_4 promoted the cotton fibers hydrolysis and carbon nucleus formation at the same time in the HTC system. In conclusion, the additive CuSO_4 is an efficient agent for synthesizing carbon microspheres by HTC from waste cotton fibers. These findings provide a new method to prepare carbon microspheres by HTC and may help researchers to understand the influence of additives on the preparation of carbon microspheres.

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Supplementary Material: The online version of this article contains supplementary material, which is available to authorized users.

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