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Structure and antibacterial activity of silver-supporting activated carbon fibers

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In this paper, several kinds of silver supporting activated carbon fibers (ACF-Ag) were prepared by the reduction adsorption on activated carbon fiber (ACF) activated with steam or H_3PO_4 using sisal, viscose and pitch fiber as precursors. Their pore structure and surface chemistry were characterized using nitrogen adsorption, XPS, WXRD and ICP quantitative analysis. Their antibacterial activities were tested. The results showed that metallic silver particle in micron or nano-scale size could be easily and dispersedly supported onto the surface of ACF using reduction property of ACF without largely decreasing their specific surface area. The ACF-Ag showed strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. The antibacterial activity has closed relationship with the precursors, the method of activation, silver content and the specific surface area of the ACFs. Generally, higher silver content and higher specific surface area provide the materials stronger antibacterial activity. ACF activated with phosphoric acid, due to the presence of certain amount of organic phosphoric groups on the surface, showed stronger antibacterial activity than those activated with steam. The antibacterial materials can be easily regenerated without decreasing their antibacterial activity and without releasing large amount of silver from the solid phase.

1. Introduction

With huge specific surface area, proper micropores and excellent adsorption capacity, activated carbon fiber (ACF) has been widely used in environmental treatment [1, 2]. However, pollutants in water contains not only chemical substances, but also microbes, which may breed on the surface of activated carbon fibers, becoming itself a pollutant and reduce the adsorption capacity of ACF; on the other hand, it is also necessary to eliminate these microbe from water for drinking water treatment. Supporting antibacterial agents, such as Ag, can not only keep the excellent adsorption capacity of ACFs, but also endow these ACFs with antibacterial activity, which will be beneficial to effective removal of organic pollutants and disinfections of drinking water.

Oya first reported a method of preparing an antibacterial activated carbon fiber, in which $AgNO_3$ was mixed with phenolic resin/or petroleum pitch, then the mixture was spun, the resulting fiber was carbonized and activated. However, the mixing of metallic compounds in the precursor resin reduce the spinnability of pitch and the tensile strength of fiber, and also suppress the development of micropore of fiber [3, 4], which reduce their adsorption capacities. Since then, other works on the preparation of antibacterial fibers and their antibacterial test have been reported [5–8].

Besides high porosity and excellent adsorption capacity for organic substance, our researches shows that ACF also can reduce some noble metal ions into low valence ion or metallic elements [9–11]. In this paper, we developed a new preparation method of Ag-supporting ACF using the reduction property of activated carbon fiber in room temperature, which can dispersedly support silver nano-particle on ACFs. Several kinds of activated carbon fibers supporting silver were prepared. Their pore structure and chemical structure were characterized. The antibacterial activities of activated carbon fibers supporting silver were quantitatively determined. And the factors that may affect their antibacterial activity were discussed.

2. Experimental

2.1. Preparation of antibacterial materials

The activated carbon fibers using viscose fiber, pitch fiber and sisal fiber as precursors were prepared by carbonization and then followed activation with steam or chemicals.

Preparation of ACF with steam activation: precursor fibers were impregnated with $(NH_4)_2HPO_4$, then

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heated up to 850°C under the protection of nitrogen for carbonization, then steam was introduced while constant temperature was kept for activation. The resulted ACF were named as mACF-*tt* (*m*—different precursor: V—viscose, P—pitch, and S—sisal fiber based; *tt*—activation time).

Preparation of ACF with chemical activation: precursor fibers were immersed with phosphoric acid. The treated fibers were heated up to 850 °C under the protection of nitrogen so as to finish carbonization and activation in one step. The resulted products were named as HPmACF-*tt* (*m*—different precursors, *tt*—activation time).

Preparation of activated carbon fiber supporting silver: above ACFs after being washed by deionized water, were immersed in silver-containing solution, and oscillating for 24 h, then the ACFs were washed with deionized water to neutral pH, the resulted samples were named as mACF - Ag (*m*—different precursor)

2.2. Structure characterization of activated carbon fiber

The specific surface areas of ACFs were characterized by means of nitrogen adsorption isotherms at 77 K on an ASAP2010 volumetric adsorption apparatus from Micromeritics (Norcross, GA, USA); the surface morphology of ACF and the distribution of silver particles on them were observed by a JSM-F6330 scanning electron microscope (SEM). The crystalline structure of silver on ACFs was examined by wide angle X-ray diffraction (WAXD) using a Rigaku D/MAX-III X-ray diffractometer. The surface chemical groups on ACF and silver valence state were analyzed by XPS method using Vacuum Generators Escalab Mk II X-ray photoelectron spectroscope. And the amount of silver in fiber was measured by Therms Jamell Ash Corporation ISIR Advantage (HR) ICP emission spectroscopy after the fiber samples were ashed and dissolved in nitric acid. The silver content releasing to the water after antibacterial test was also determined by ICP method.

2.3. Antibacterial test

The antibacterial activities of silver supporting activated carbon fibers were estimated by its inhibitory and sterilized effect against *E. coli* (ATCC 25922, *Escherichia coli*) and *S. aureus* (ATCC 6538, *Staphylococcus aureus*). 50 mg of the above sample was transferred into a flasks, then 10 ml 1/10AATCC nutrition broth and 10 ml physiological saline (pH = 7.0–7.2) were added to each flask. These samples were sterilized for 20 min under 0.1 MPa pressure. Once the solution cooled down to the room temperature, the bacterium was inoculated into the flask. The flasks with ACFs and bacterium were shaken at 37°C for different periods. Surviving bacteria in the solution after contacting with ACF-Ag was counted by spread plate culture method: 0.1 ml of the solution of the bacterial suspension in the flask was taken out, and inoculated in culture medium of nutrient agar, and incubated in a constant temperature box at 37°C for 24 h. Then the survival amount of bacteria (cfu/mL) was counted from the colony formed on the medium. All the initial concentrations of bacteria or survival amounts of bacteria after test were calculated based on the colony number on culture plate of the dilute solution. In all antibacterial tests, a blank reference (without antibacterial materials) for each test has been done.

3. Results and discussion

3.1. Structure of ACF and ACF-Ag

The pore volume and specific surface area of ACFs was determined based on their nitrogen adsorption isotherms at 77 K; typical results of SACF were shown in Table I. It is clear that the specific surface area (S_{BET}) of SACF is around 1200 m^2/g, and the total pore volume (V_t) is more than 0.6 cm^3/g, and most pores are micropores, the peak distribution of micropore diameter is around 0.8 nm, and the mean diameter (D_{micro}) of micropore are in the range of 0.59 to 0.73 nm. The specific surface areas of all other sets of activated carbon fibers using sisal fiber, or pitch fiber as precursors are in the range of hundreds to over 2000 m^2/g depending on the preparation condition, such as activation time, temperature, and activation chemical agent and their concentration) (Table I).

It would be pointed out that the reaction between H_2O and carbon on SACF-90 would be more drastic because of the higher flux of water vapor for the activation of this sample, which resulted in the broadening and even collapse of micropores. As a result, SACF-90 showed higher pore volume and a slight lower specific surface area than those of SACF-120 though activated for a longer time.

In HPSACF series, when precursor fibers were heated to 850°C, carbonization and activation occurred in one step, the formation of micropore makes the HPSACF have high surface area. And if it is further heated

TABLE I Parameters of porosity of ACFs

Samples	S_{BET} (m^2/g)	V_t (cm^3/g)	Mean D_{micro} (Å)	Samples	S_{BET} (m^2/g)	V_t (cm^3/g)	Mean D_{micro} (Å)
SACF-30	1203	0.603	5.9	HPSACF-0	1351	0.681	6.3
SACF-60	1371	0.691	6.2	HPSACF-30	1213	0.615	5.9
SACF-90	1244	0.802	7.3	HPSACF-50	1217	0.600	5.8
SACF-120	1308	0.661	6.3	HPSACF-80	1186	0.588	5.8
PACF-120	2251	1.187	7.3	HPPACF30	2		
PACF-90	2076	1.054	7.1	HPPACF60	52		
PACF-60	2246	1.205	7.2	HPPACF90	189	0.094	5.1
PACF-30	1359	0.650	6.1	HPPACF120	700	0.317	5.5

TABLE II Comparison of pore Parameters of VACF before and after silver supporing

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{Micro} (cm^3/g)	D_{Avg} (Å)	D_{Micro} (Å)
VACF-30	1243.1	0.602	0.546	19.4	6.0
VACF-30-Ag (Total materials)	812.6	0.409	0.357	20.1	6.1
VACF-30-Ag (Carbon only)	1041	0.524			
VACF-50	1114.0	0.542	0.507	19.5	5.4
VACF-50-Ag (Total materials)	872.8	0.429	0.380	19.6	5.7
VACF-50-Ag (Carbon only)	1091	0.536			
VACF-90	1928.4	1.016	0.634	21.1	7.2
VACF-90-Ag (Total materials)	1336.6	0.680	0.525	20.4	6.5
VACF-90-Ag (Carbon only)	1670	0.85			

at constant temperature 850°C for a longer time, carbon atoms would rearrange to form more ordered graphite crystal, and result in the slight shrinking of pore and a decrease of specific surface area of ACF.

Comparison of pore parameters of ACF before and after silver supporting shows that the specific surface area, total pore volume and micropore volume (V_{Micro}) of ACFs will have a little decrease after silver supporting, which means that part of silver particles would fill in the inner micropore of ACF. A typical comparison of porosity parameters of VACFs that supported about 20 wt% silver is shown in Table II. If based on total materials (ACF plus silver supported), the specific surface area have a 30% drop, however, there is about 10 to 15% decrease if based on carbon materials only. Similar reasons are for the total pore volume. The comparison of average pore diameter (D_{Avg}, 4 V/A BET) or mean micro-pore diameter (D_{Micro}) shows that the silver supporting have little change in their pore size distribution except a slight decrease in quantity. Compared to the specific surface area of ACF prepared by mixing silver compound with precursor polymer [3, 4], silver supporting ACFs prepared by the method described in this article still keep very high specific surface area, which is beneficial to their high adsorption capacity for organic pollutants.

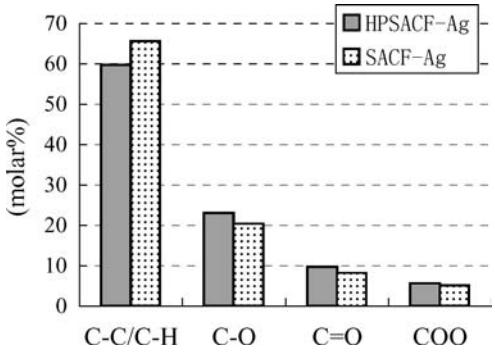

Figure 2 The relative content of carbon groups in HPSACF-Ag and SACF-Ag surface.

Basing on XPS of C1s, the surface chemistry of the samples was analyzed. C1s spectra is divided into 4 components which correspond to the C=C or C–H (binding energy 284.6 eV), C–OH (hydroxyl group, 286.1 eV), C=O or O–C–O (carbonyl or ether group, 287.7 eV), and COOH (carboxyl group, 289.8 eV) (Fig. 1). The Curve processing results of C1s spectra of a typical SACF sample show the molar percentage of these groups on SACF are C=C/C–H 64.33%, hydroxyl group 26.48%, carbonyl group 7.06, and carboxyl group 2.12%, respectively. And the typical results of SACF-Ag are C=C/C–H 55.56%, hydroxyl group 27.53%, carbonyl group 11.80, and carboxyl group 5.11%, respectively. The O/C atomic ratio on ACF increase from 0.17 for HPSACF without supporting silver to 0.27 for HPSACF-Ag after supporting silver, which would indicate that surface carbon on ACF had been oxidized to oxygen-containing groups such as hydroxyl, carbonyl, or even carboxyl groups. Comparison of O/C ratio for SACF and SACF-Ag also showed similar result, O/C ration for SACF was 0.20, and that for SACF-Ag was 0.27, this result also revealed the oxidation of surface carbon.

The comparison of the above data sets before and after silver adsorption shown that the proportion of

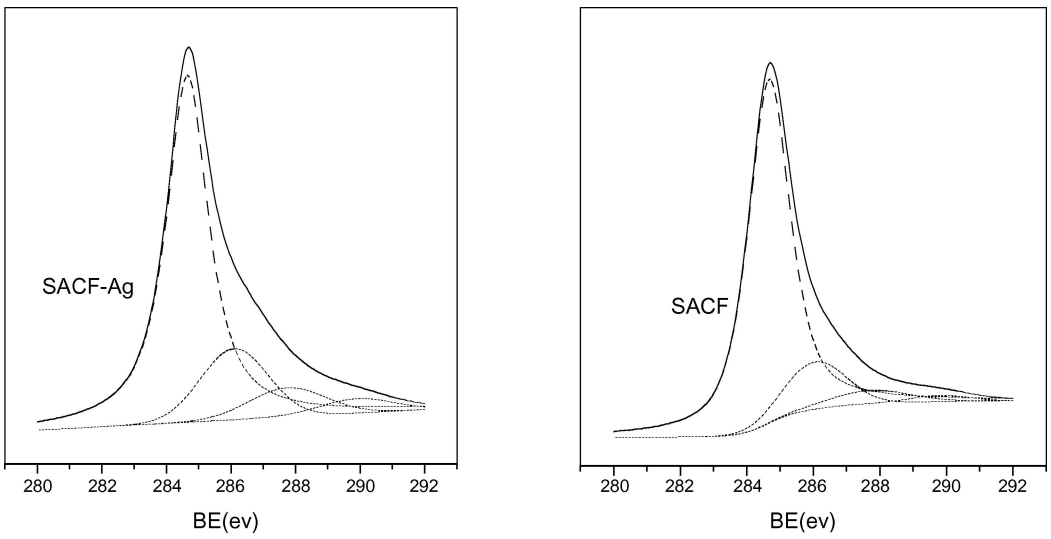

Figure 1 C_{1s} XPS spectra of SACF-Ag and SACF.

C=C/C–H in total carbon evidently decrease, but the proportion of C–O, C=O/O–C–O, COOH groups evidently increase, which indicate that the C–H on ACF surface has been oxidized into higher valence groups such as hydroxyl, carbonyl, or carboxyl groups, the typical reaction would be:

$$\mathrm{ACF} \sim \mathrm{C-H} + 2\mathrm{Ag}^{+} + \mathrm{H_2O} \rightarrow \mathrm{ACF} \sim \mathrm{C-OH} + 2\mathrm{Ag} + 2\mathrm{H}^{+}$$

ACFs prepared by different methods showed similar surface chemical group composition, however, the percentage of oxygen-containing groups has a slight variation. Fig. 2 shows the atomic composition of surface groups of SACF-Ag and HPSACF-Ag, it is clear that there are more oxygen-containing groups on HPSACF-Ag than those on SACF-Ag. The reduction behavior and mechanism of silver ion by ACF have been discussed in our previous papers [9–11].

Fig. 3 shows the XPS spectra of $Ag3d_{5/2}$ and Ag_{MNN}. The binding energy of $Ag3d_{5/2}$ is 368.3 eV, and the kinetic energy of Ag_{MNN} is 357.4 eV, thus the Auger parameter α' ($= E_k$ (Auger electron) $+ E_B$ (photo electron)) is equal to 725.7 eV, which means most of the silver on ACF present in a 0 valence (metallic silver),

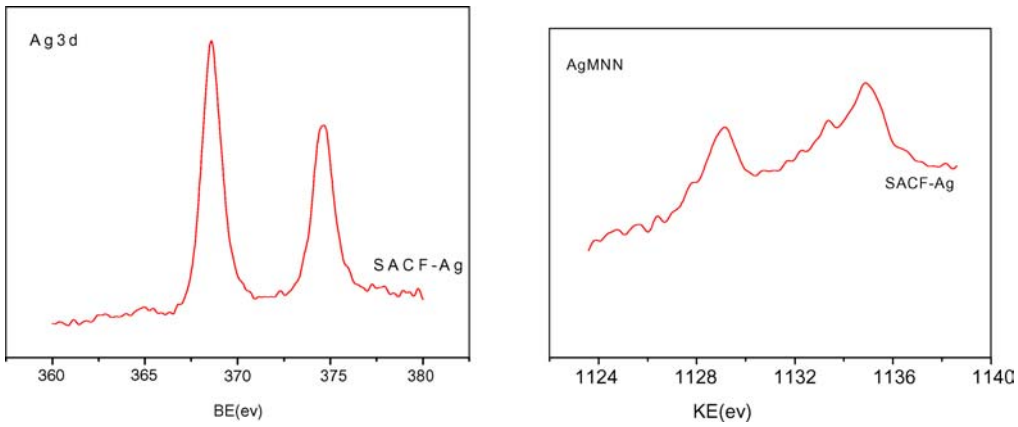

Figure 3 Ag_{3d} and Ag_{MNN} spectra of SACF-Ag.

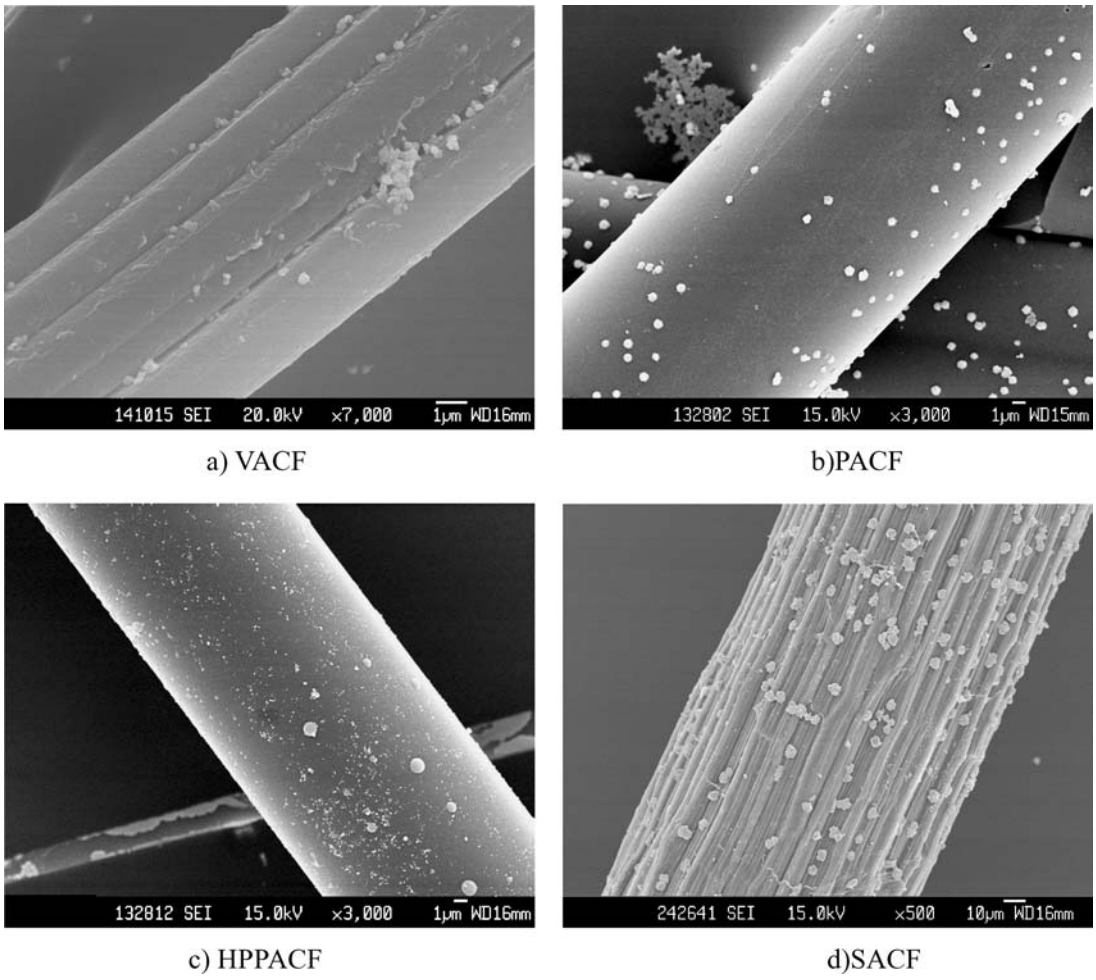

Figure 4 Distribution of silver particle on activated carbon fibers.

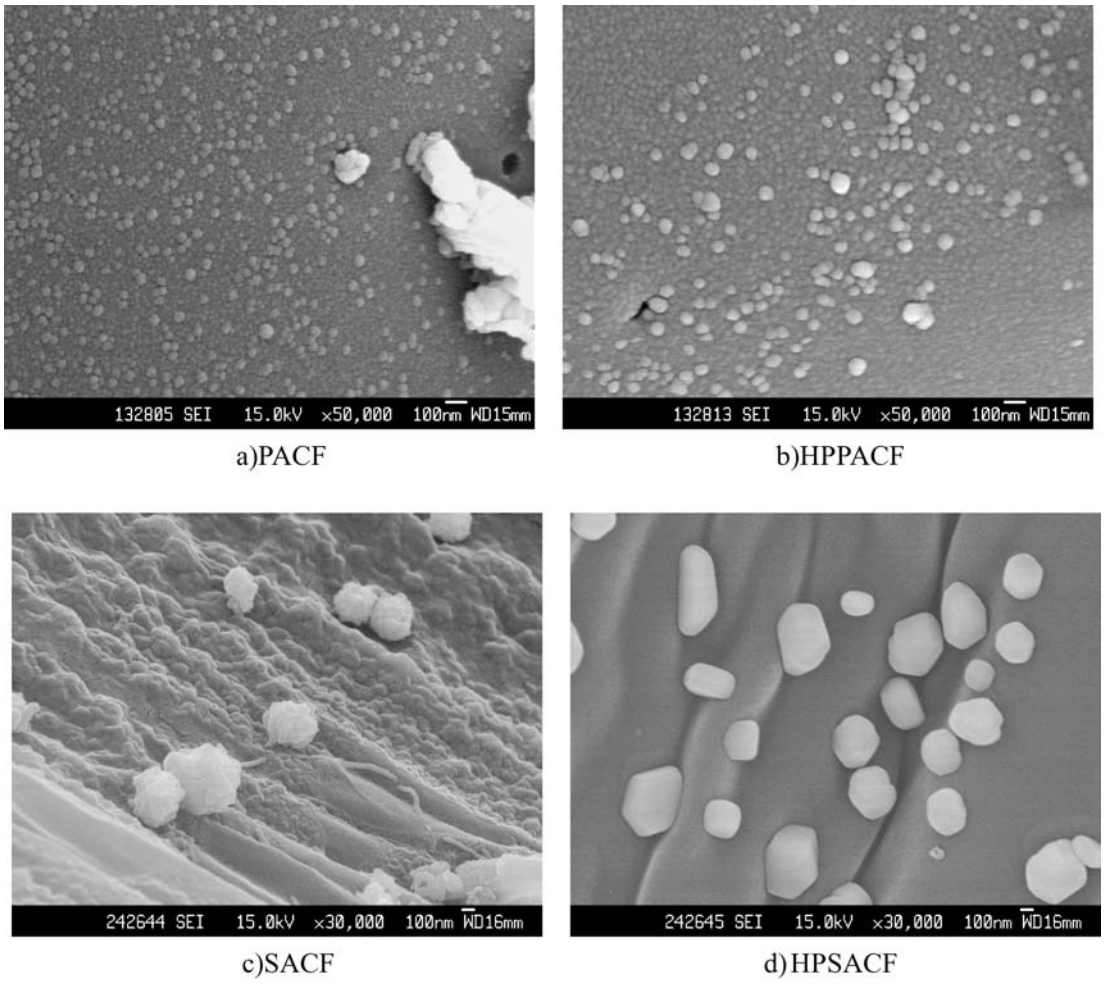

Figure 5 Nano-particle of silver on ACF.

for the Auger parameter α' is equal to 726 eV for 0 valence silver, and 1 valence silver is 724.5 eV.

From the SEM images, lots of silver particles can be clearly observed (Fig. 4). Most of the silver particles are distributed on the external surface of ACF. The above pore structure analysis has also revealed that part of silver particles would fill in the inner micropore of ACF. Fig. 4 also shows that silver particles on VACF or on PACF are much smaller than those on SACF. In larger scale SEM photos, it is clear that besides the micrometer-scale silver particles there are also much finer particles on the surface of ACFs, which are on dozens of nanometer scale (Fig. 5).

Fig. 6 shows the X-ray diffraction pattern of SACF-Ag prepared by different activation duration. There are 4 diagnostic sharp diffraction peaks, which correspond to the diffraction of (111), (200), (220) and (222) of metallic silver crystal, which evidently reveals that silver ions in solution have been reduced to 0 value metallic silver by ACFs.

All of above results clearly indicate that silver ions have been adsorbed and reduced to metallic element, which deposited at micron to nano-scale particles on the ACFs.

3.2. The antibacterial activity comparison of ACFs derived from different precursors

The antibacterial activity test of silver supporting activated carbon fiber derived from different precursors

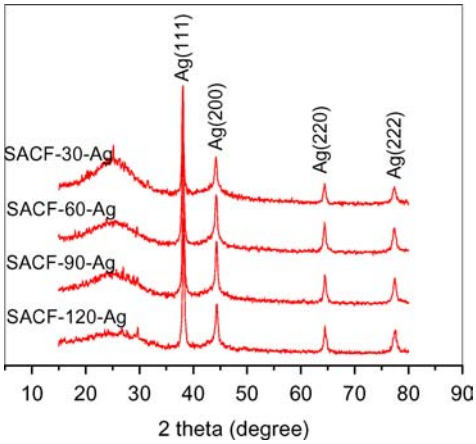

Figure 6 WARD pattern of SACF-Ag prepared by different activation duration.

was shown in Table III. It indicated that among the several activated carbon fibers prepared by steam at 850°C, sisal-based activated carbon fibers showed the best antibacterial activity, which can completely kill *E. coli* at the concentration of 5×10^8 cfu/ml in 8 h, while in the same condition, there was uncountable *E. coli* surviving in the solution that contacted with viscose based or pitch based ACF. Because sisal based ACF could inherit the vegetable structure and coarse surface from its precursor—sisal fiber (Figs 4 and 5), they would have higher affinity to bacteria in solution, thus

TABLE III Antibacterial test against *E. coli* of Ag-supporting ACF derived from different precursors*

Sample	Initial count of bacteria in solution (cfu/ml)	Bacteria count in solution after testing (cfu/ml)**
VACF-30-Ag	1×10^8	*uc*
VACF-50-Ag		*uc*
VACF-70-Ag		*uc*
VACF-90-Ag		*uc*
Blank reference***		*uc*
PACF-30-Ag	1×10^8	*uc*
PACF-60-Ag		*uc*
PACF-90-Ag		*uc*
PACF-120-Ag		*uc*
Blank reference		*uc*
SACF-30-Ag	5×10^8	0
SACF-60-Ag		0
SACF-90-Ag		0
SACF-120-Ag		0
Blank reference		*uc*

*contact time = 8 h, pH of solution = 7.0, bacterial: *E. coli*.
***uc*—countless bacteria on the culture plate (the same for others).
****Blank reference*—no antibacterial material (the same for others).

TABLE IV Ag-type ACF antibacterial test against *S. aureus*

Sample	Initial count of bacteria in solution (cfu/mL)	Contact time (h)	Bacteria count in solution after testing (cfu/mL)
SACF-Ag	1×10^7	18 h	0
VACF-Ag			0
SACF	1×10^7	18 h	*uc*
VACF			*uc*

there is higher probability for silver particles on SACF to contact and kill the bacteria. On the contrary, VACF and PACF have much smoother surface, and their hydrophobic properties make it a little difficult for silver particles on them to contact bacteria in solution, which makes these kinds of ACF own less antibacterial activity than SACF.

Table IV shows the antibacterial activities against *S. aureus* of Ag supporting ACF. From the results of the antibacterial test, it is evident that these Ag-type ACFs have also strong antibacterial activity against *S. aureus*. While supporting certain amount of silver, they could kill all *S. aureus* in the solution, at the same condition there was countless *S. aureus* survived in the solution while contacting with ACF without silver supporting.

3.3. The influence of the silver content on the antibacterial activity

In order to obtain different silver supporting content VACF, five portions of same viscose based activated carbon fiber (VACF-50) carbonized and activated at 850°C for 50 min were immersed in different concentration of silver solutions. The silver contents supported on the resulted VACF, measured with ICP emission spectroscopy, are from 0.08 to 10.64 wt%. Their antibacterial activities were compared in Table V. The result showed that the antibacterial activity of the activated carbon fibers became stronger with the increase

TABLE V Effect of silver content on the antibacterial activity of activated carbon fibers

Sample	Ag content (wt%)	Bacteria count in solution after testing (cfu/ml) A	B
VACF-50-Ag-1	0.08	*uc*	*uc*
VACF-50-Ag-2	0.25	*uc*	*uc*
VACF-50-Ag-3	2.13	*uc*	*uc*
VACF-50-Ag-4	5.21	400	170
VACF-50-Ag-5	10.64	30	10
Blank reference		*uc*	*uc*

Initial count of *E. coli* in solution = 5×10^7 cfu/ml, contact time = 8 h, pH7.0; *A, B*—paralleling analysis (the same for others).

of the silver content in the activated carbon fiber, and when the silver content rose to about 5 wt%, it could kill all of *E. coli* in solution, which indicates that silver on ACF is the effective component for bacteria-killing.

The effect of silver content on antibacterial activity for another kind of ACF activated by phosphoric acid is shown in Table VI. Same weight of ACF with different silver supporting content were added to the *E. coli* solution and were shaken for 2 h, the number of *E. coli* survived for each series with the same initial concentration of bacteria is listed in Table VI. The results in Table VI clearly show that antibacterial activity increase with the silver content in ACF. The comparison of different initial concentration of bacteria shows the same tendency, the only difference is that for the same sample (for example, HPSACF-80-Ag-3) at the same condition, nearly all bacteria in the solution were killed while the initial concentration of bacteria is lower, and much more bacteria survived while the initial concentration of bacteria is higher.

3.4. Antibacterial effective time of ACF-Ag

Table VII shows the antibacterial activity against *E. coli* of silver-supporting SACF activated by phosphoric acid. It indicated that all these Ag supporting ACFs could completely kill all *E. coli* in 20 mL solution with the concentration of $10^6 \sim 10^7$ cfu/ml in 2 h. Table VII also shows the antibacterial results in shorter contact time. The results shows that for ACF with less silver supporting content such as HPSACF-0-Ag it would take a longer time to kill all bacteria in solution, and for ACF with more silver in it such as HPSACF-80-Ag it would take a shorter time to kill all bacteria in solution. The above result also implies that the antibacterial effective time is also determined by the concentration of bacteria in solution. For lower concentration of bacteria, it would take less time, and for city water supply that usually contain only several to tens bacteria it would take far less time to kill them with these kinds of antibacterial materials.

3.5. The influence of the specific surface area of ACF on the antibacterial activity

A set of activated carbon fiber supporting the similar amount of silver but with different specific sur-

TABLE VI Effect of silver content in HPSACF on their antibacterial activity

Sample	The silver percent (wt%)	Initial count of *E. coli* in solution (cfu/ml)					
		1×10^5		1×10^6		1×10^7	
		Bacteria count in solution after testing (cfu/ml)					
		A	B	A	B	A	B
HPSACF-80-Ag-1	~ 0.3	*uc*	*uc*	*uc*	*uc*	*uc*	*uc*
HPSACF-80-Ag-2	1.43	*uc*	*uc*	*uc*	*uc*	*uc*	*uc*
HPSACF-80-Ag-3	5.14	0	40	820	400	*uc*	*uc*
HPSACF-80-Ag-4	5.37	0	0	0	0	820	540
HPSACF-80-Ag-5	15.5	0	0	0	0	430	280
Blank reference		*uc*	*uc*	*uc*	*uc*	*uc*	*uc*

Contact time = 2 h, pH of the solution = 7.0.

TABLE VII antibacterial result for different contact time

Contact time (h)	0.5		1		1.5		2	
	A	B	A	B	A	B	A	B
HPSACF-0-Ag	*uc*	*uc*	*uc*	*uc*	*uc*	0	0	0
HPSACF-50-Ag	*uc*	*uc*	*uc*	*uc*	420	630	0	0
HPSACF-80-Ag	*uc*	*uc*	200	160	0	0	0	0
Blank reference	*uc*	*uc*	*uc*	*uc*	*uc*	*uc*	*uc*	*uc*

Initial count of *E. coli* in solution = 5×10^6 cfu/ml; pH = 7.0.

face area was prepared. Their antibacterial activities against *E. coli* at different initial concentration of bacteria (5×10^4 to 5×10^7) were tested. The results in Table VIII show that the antibacterial activity of the silver-supporting activated carbon fiber increased correspondently with their specific surface areas. HPPACF-30-Ag, having only 2 m^2/g of Specific Surface Area, showed very weak antibacterial activity, there was still countless *E. coli* surviving in the solution after being shaken for 8 h even in the case of lower initial concentration of *E. coli* (5×10^4 cfu/mL); In the same condition, other samples with higher surface area could kill all bacteria in the solution. Similar results were observed in the cases with higher initial concentration of bacteria, HPPACF-90-Ag and HPPACF-120-Ag with higher specific surface area can kill all bacteria in solution when the initial concentration of bacteria is as high as 5×10^7 cfu/mL, but in the same condition, there was still countless *E. coli* surviving in the solution which contacted with HPPACF-30-Ag and HPPACF-60-Ag with lower specific surface area. We could deduce from the results that the surface of the activated carbon fiber provide plentiful surface to adsorb bacteria. The bacteria were first converged on the materials surface, and the silver supported on the ACFs will catalyze H_2O to form such kinds of active components as radical hydroxyl (·OH) and active negative oxygen ions (O_2^-), which inhibit the growth of bacteria or kill them.

TABLE VIII Effect of surface area on antibacterial activity against *E.coli*

Sample	Specific surface area (m^2/g)	Initial count of bacteria in solution (cfu/ml)			
		5×10^4	5×10^5	5×10^6	5×10^7
		Bacteria count in solution after testing (cfu/ml)			
HPPACF-30-Ag	2	*uc*	*uc*	*uc*	*uc*
HPPACF-60-Ag	52	0	0	10	*uc*
HPPACF-90-Ag	197	0	0	0	0
HPPACF-120-Ag	652	0	0	0	0
Blank reference		*uc*	*uc*	*uc*	*uc*

Contact time = 8 h, solution pH = 7.0.

3.6. Effect of activation agent of ACF on their antibacterial activity

Antibacterial activities of silver supporting pitch based activated carbon fibers activated with steam (PACF-Ag) and activated with phosphoric acid (HPPACF-Ag) were compared in Table IX. The results show that the activated carbon fiber activated by phosphoric acid preceded in antibacterial activity to activated carbon fibers activated by steam, and that the silver-supporting activated carbon fibers activated by phosphoric acid could completely kill the *E. coli* at the concentration of 1×10^8 cfu/ml in the solution, however, there were countless *E. coli* surviving in solution when contacting with PACF-Ag. Similar results were observed for another set of samples, sisal based ACFs activated with steam (SACF-Ag) and activated with phosphoric acid (HPSACF-Ag). Silver supporting sisal based ACF acti-

TABLE IX Comparison of antibacterial activity of PACF-Ag and HPPACF-Ag

Sample	Bacteria count in solution after testing (cfu/ml)	
	A	B
PACF-30-Ag	*uc*	*uc*
PACF-60-Ag	*uc*	*uc*
PACF-90-Ag	*uc*	*uc*
PACF-120-Ag	*uc*	*uc*
HPPACF-30-Ag	*uc*	*uc*
HPPACF-60-Ag	0	0
HPPACF-90-Ag	0	0
HPPACF-120-Ag	0	0
Blank reference	*uc*	*uc*

Initial count of *E. coli* in solution = 1×10^8 cfu/ml, contact time = 8 h, solution pH = 7.0.

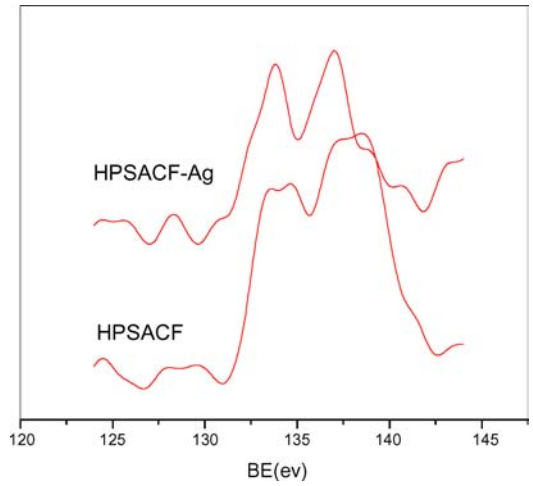

Figure 7 P_{2p} spectra of HPSACF-Ag and HPSACF.

vated with phosphoric acid have stronger antibacterial activities than those activated with steam. At the same condition, HPSACF could kill all 1×10^8 cfu/ml *E. coli* in the solution, however, there is countless *E. coli* surviving in solution while contacting with SACF-Ag.

The difference of antibacterial activities between ACFs activated with phosphoric acid and ACFs activated with steam may due to the surface chemical structure of them. Fig. 7 shows the XPS spectra of P_{2p} on ACF before and after silver supporting. Generally, the binding energy for organic phosphor is between 131–135 eV, and the peak near 137 eV would represent the P_2O_5 [12]. The XPS in Fig. 7 evidently indicate the presence of these two phosphor forms. And the slight shift of P_{2p} to lower binding energy would mean the combination of silver ions with phosphor on ACF surface. It is well known that organic phosphoric compounds are excellent antibacterial agent, therefore, it would be deduced that the presence of certain amount of phosphor-containing groups on ACF would serve as antibacterial groups that would inhibit the growth or destroy the bacteria cell, and enhance the antibacterial activity of HPACF.

From above Fig. 2 we also know that, though most silver on ACF is metallic element, there is still a small amount of silver may present in ionic state on the ACF surface for the Auger parameter α' is still less than 726 eV (for 0 valence silver). Dissociative silver ions may easily combine with cell of bacteria and destroy them. The presence of silver ions or silver organic phosphor compounds on ACF activated with phosphoric acid would also induce the formation of active oxygen, or slowly release silver ion to destroy the bacterial cell. Both of these silver ion itself or silver organic phosphor compounds thus improve the antibacterial activity of ACF prepared by phosphoric acid activation.

Moreover, a set of silver supporting HPSACFs, activated by different concentrations of H_3PO_4, were prepared, their antibacterial activity against *E. coli* at the same condition was shown in Table X. The results in Table X indicated that the concentration of activation agent did affect their antibacterial activity. Their antibacterial activity increased accordingly with concentration of phosphoric acid activation agent, and when

TABLE X The antibacterial activity of HPSACF-Ag activated by different concentration of H_3PO_4

Sample	Concentration of H_3PO_4	Bacteria count in solution after 2 h (cfu/ml)		Bacteria count in solution after 4 h (cfu/ml)	
		A	*B*	*A*	*B*
HPSACF- 5%-Ag	5%	*uc*	*uc*	670	650
HPSACF-10%-Ag	10%	*uc*	*uc*	40	10
HPSACF-20%-Ag	20%	*uc*	120	10	40
HPSACF-35%-Ag	35%	0	0	0	0
Blank reference		*uc*	*uc*	*uc*	*uc*

Initial count of *E. coli* in solution = 5×10^7 cfu/ml, solution pH = 7.0.

the contact time extended to 4 hrs., nearly all *E. coli* in solution with concentration of 5×10^7 cfu/ml could be completely killed by the silver supporting HPSACFs. The reason may be that the HPSACF activated with high concentration of phosphoric acid will have higher content of phosphor-containing groups on the surface, and have higher surface area; both of them are benefit to increase their antibacterial activity.

3.7. Regeneration of antibacterial materials and silver amount released

The regeneration of antibacterial materials could be done by simply washing the silver supporting ACF with deionized water after antibacterial test. Table XI shows the antibacterial activity of materials regenerated. The results indicate that silver supporting ACF still showed strong antibacterial activity after regeneration of 5 times, it could completely kill 10^7 cfu/ml *E. coli* as the original materials did.

As disinfecting materials for drinking water purification, the silver-supporting ACF must be able to firmly hold silver on the solid phase, that is, the silver release amount from the material must be very low to keep their antibacterial activity and to meet the requirement of the quality standard of drinking water (Ag content < 50 ppm). Table XII shows the silver amount released from ACF samples after 50 mg of silver supporting ACFs were soaked in 50 ml water and shaken for 2 to 6 hrs. The maximum amount is around 10 ppm, which meets the quality standard of drinking water. Indeed, for large amount of running water treatment, the silver concentration will be still lower.

TABLE XI Regeneration of Ag-supporting ACF

Regeneration times	Initial count of *E. coli* in solution (cfu/ml)	Bacteria count in solution after 2 h (cfu/ml)	
		Without HPSACF-80-Ag	Contact with HPSACF-80-Ag
1	2×10^6	4×10^6	0 0
2	5×10^6	6×10^7	0 0
3	2×10^8	1×10^9	10 0
4	1×10^8	3×10^8	0 0
5	1×10^7	2×10^7	0 0

TABLE XII The release of silver content from the SACFs as a function of the time

Sample	Ag supporting amount (wt%)	Ag released (ppm)		
		2 h	4 h	6 h
1	5.85	4.8	6.1	6.0
2	9.8	6.1	10.4	10.1
3	13.3	4.2	5.6	5.4
4	13.65	7.4	8.4	7.2
5	15.25	5.6	6.8	8.7

4. Conclusion

1. Silver supporting activated carbon fiber with high antibacterial activity could be prepared by simply impregnating the fiber in silver-containing solution using their reduction property and high surface area to reduce silver ion into metallic element and adsorb them on the surface. The silver particles dispersedly present in surface of ACF at micron to nano-scale particles.

2. These kinds of silver supporting activated carbon fiber show strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. Metallic silver on activated carbon fibers is an effective antibacterial component that may induce the formation of active oxygen group to inhibit bacteria growth or kill them. With the increase of silver amount supported on ACF, the antibacterial activity of materials increases. Trace amount of organic phosphoric group and silver ions on activated carbon may enhance their antibacterial activities because of serving directly themselves as antibacterial components.

3. Higher specific surface area of ACF is benefit to their antibacterial activity, which provides plentiful surface to adsorb bacteria and for silver to contact effectively with bacteria.

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