Effect of carbon fiber surface treatment on Cu electrodeposition: The electrochemical behavior and the morphology of Cu deposits

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ABSTRACT

The relationship between surface functional groups and electrochemical behaviors of polyacrylonitrile (PAN)-based carbon fibers (CFs) differentiated by oxidation treatment in air was studied. The chemical character of the CFs surface was estimated by X-ray photoelectron spectroscopy (XPS) and the electrochemical behavior of treated CFs in $CuSO_4$ plating solution was studied by electrochemical setup. The influence of functional groups on the morphology of copper deposits was characterized by field-emission scanning electron microscopy (FESEM). It was found that the O/C atomic ratio rose rapidly from 23.05% (as-received carbon fibers) to 42.83% as the oxidation temperature was increased to 400 °C and the content of –C═O was the highest. Concentrations and types of the functional groups on CFs surface showed a close connection with the electrochemical response of CFs in $CuSO_4$ plating bath. It was showed that Cu electrodeposition was the interaction of applied voltage and the reduction of surface functional groups. With the functional groups increased, the quantities of the Cu nuclei increased, further the morphology of deposited Cu was affected.

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1. Introduction

Carbon fibers have been widely used for many years due to their lightweight, durable and good performance [1,2]. Since untreated carbon fibers exhibit very low wettability [3], surface treatment is an important step to develop the surface area or functional groups to improve the wettability of the fiber surface [4]. The surface treatments of CFs include electrochemical oxidation [5], wet oxidation usually in the strong oxidants, such as concentrated nitric acid, sodium hydroxide or sulfuric acid [6] and ammonia [7], and gaseous oxidation including oxygen or a gas mixture of oxygen and nitrogen [8], and ozone oxidation [9] as well as plasma treatments [10].

The deposition of metals on carbon fibers is important for the manufacture of composites [6]. Tzeng et al. [11] electroless deposited copper and nickel onto the carbon fiber and prepared Cu- and Ni-coated carbon fiber-reinforced ABS composites. They found that among the metal-coated carbon fibers/ABS composites, electroless nickel-coated carbon fibers/ABS composites showed the best EMI shielding capability. Lu et al. [12] electroplated Ni over the surface of CFs. The resistivity of Ni-coated carbon fibers decreased with an increase in plating time. They prepared the composites of Ni-coated carbon fibers in ABS resin and the shielding effectiveness of ABS resin filled with 10 vol.% of Ni-coated carbon fibers was

about 50 dB. They summarized that the use of Ni-coated carbon fibers as filler could greatly decrease the required volume fraction of fibers. Tang et al. [13] copperized CFs by a new electrodeposition technology. The CFs with Cu coatings were used to prepare copper matrix composites directly. Yang et al. [14] fabricated Fe-coated carbon fibers by an electrochemical method. It was found that Fe-coated fiber-epoxy composites exhibited a high value in the frequency range of 2–18 GHz, due to the longer conducting length of the fiber and the good conductivity of the iron.

Copper is the most common one of the metals since its importance in many industrial fields [15], and Cu electrodeposition has been studied for a long time. While to the best of our knowledge, the influences on the electrochemical behaviors and the morphology caused by the surface chemistry of CFs have not been reported mostly. Thus the aim of our investigation is to examine the relationship between the three ones: the functional groups on CFs surface, the electrochemical activity of CFs in $CuSO_4$ plating bath and the morphologies of copper deposits. The obtained samples could be assumed as model material for studying the influence of surface chemistry on the electrodeposition process.

2. Experimental

The PAN-based carbon fiber was T300 made by Shanghai Qijie Carbon Material Co. Ltd. in China. The properties of carbon fibers were: density 1.76 g/cm³, average diameter 7 μm. The oxidation temperatures were 200, 300 and 400 °C in air.

A Kratos Axis Ultra[DLD] X-ray photoelectron spectrometer was used in order to evaluate the as-received and treated carbon fibers. The monochromatized Al Kα X-ray source (1486.6 eV) was applied to generate core excitation operated at

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15 kV and 10 mA. The scanning condition for survey measurement was 150 ms/step, 50 meV/step and 3 sweeps. For calibration purposes, the principal C 1s electron bond energy was 284.8 eV (±0.48 eV energy resolution of the spectrometer at the setting employed). The spectra were analyzed and processed with the use of CasaXPS software. The peak shape chosen was Gaussian with a 30% Lorentzian contribution. Shirley backgrounds were applied to across the fitting regions prior to peak fitting, and individual components were assumed symmetric and without tailing factors.

50 g/L $CuSO_4$ adsorption solution was prepared with deionized water for blank experiments. Salt used was $CuSO_4 \cdot 5H_2O$ for Cu(II) with chemical purity. The as-received and treated carbon fibers were immersed in the adsorption solution with magnetic stirring for 40 h. The samples were then dried in vacuum at 105 °C.

Electrochemical setup was a standard three-electrode cell. The CFs were the working electrode and fixed on a conductive substrate connected with conducting wire. Pt was the counter electrode, and saturated calomel was the reference electrode. Experiments were carried out in a sulfate bath. The composition of the composite plating bath was 50 g/L $CuSO_4 \cdot 5H_2O$ + 10 g/L sodium tartrate + 90 g/L sodium citrate + 12 g/L KNO_3. All experiments were performed under constant temperature conditions ($T = 25$ °C) and pH was about 4.7.

The electrodeposition was in the above plating bath. A homogeneous dispersion of CFs was achieved by the addition of polyethylene glycol (mean molecular weight 5000; PA5000) to the $CuSO_4$ bath. Plating was performed at room temperature with magnetic stirrer. A copper plate containing phosphorus (JISH 3250) was used as the anode. The specification of the experimental procedure was given in Ref. [16] and the mechanics of CFs electrodeposited Cu was illuminated in Ref. [17].

Surface morphology was characterized by field-emission scanning electron microscopy (Fei Sirion 200/Inca Oxford, Fei/Oxford Co. Ltd.).

3. Results and discussion

3.1. Effect of the pretreatment of CFs

The XPS survey spectra (shown in Fig. 1) of as-received and treated CFs are recorded to identify the chemical composition of the surfaces. This was taken for all the samples prior to individual elemental scans (C 1s and O 1s). The major peaks in the
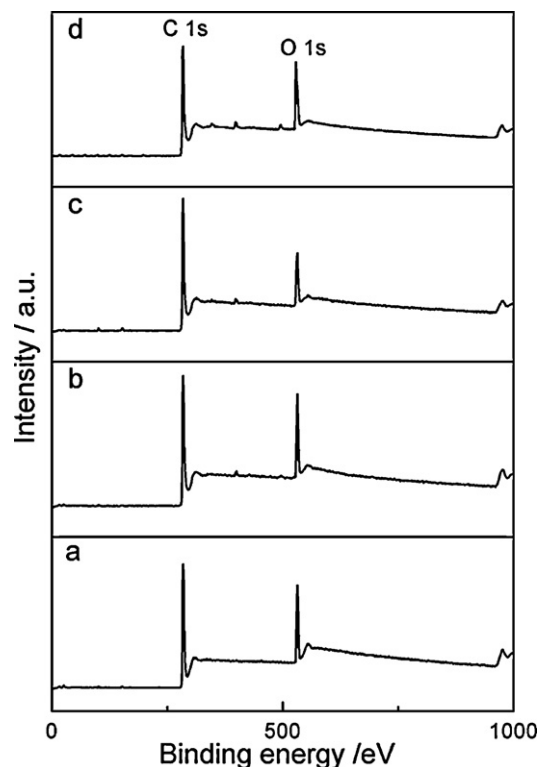

Fig. 1. XPS survey spectra of (a) as-received CFs, (b) 200 °C treated CFs, (c) 300 °C treated CFs and (d) 400 °C treated.
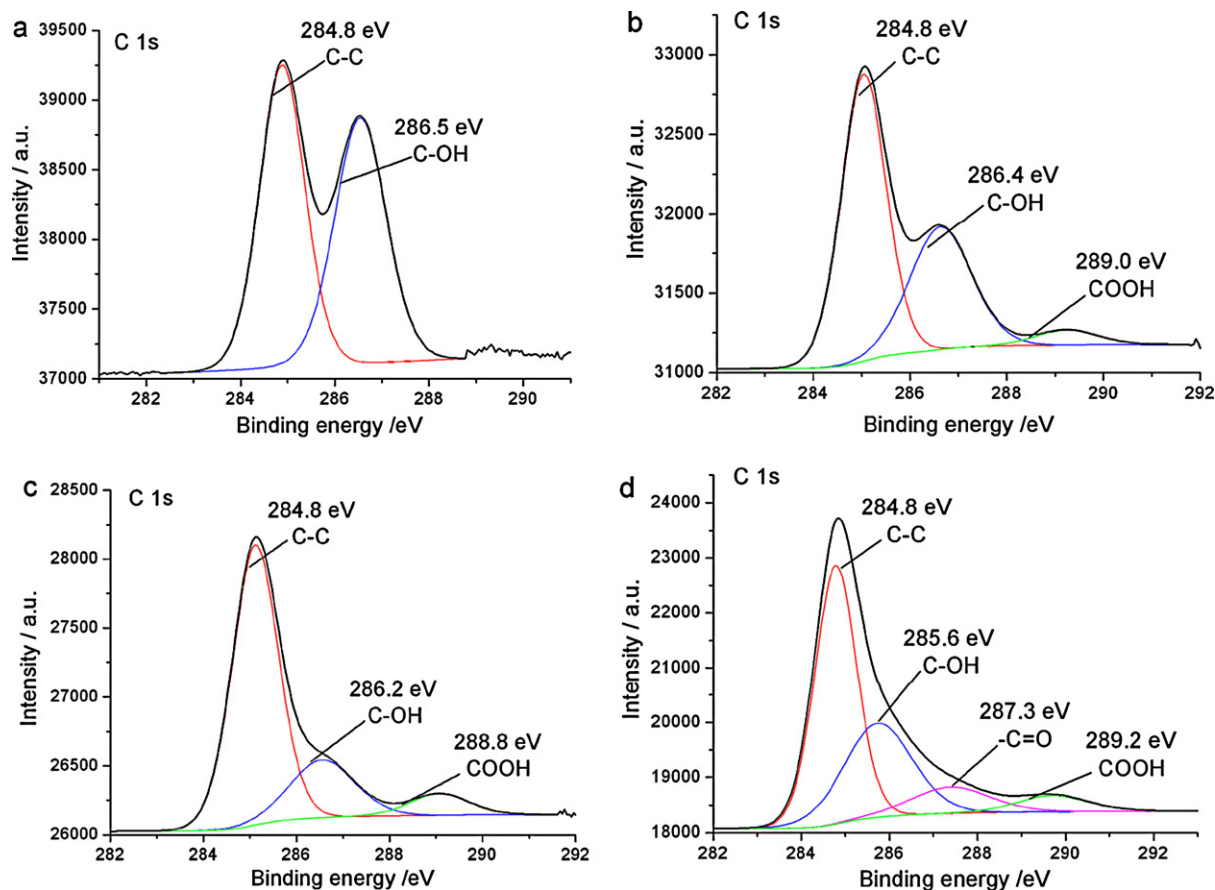

Fig. 2. The curve fitting of C 1s spectra of (a) as-received CFs, (b) 200 °C treated CFs, (c) 300 °C treated CFs and (d) 400 °C treated.
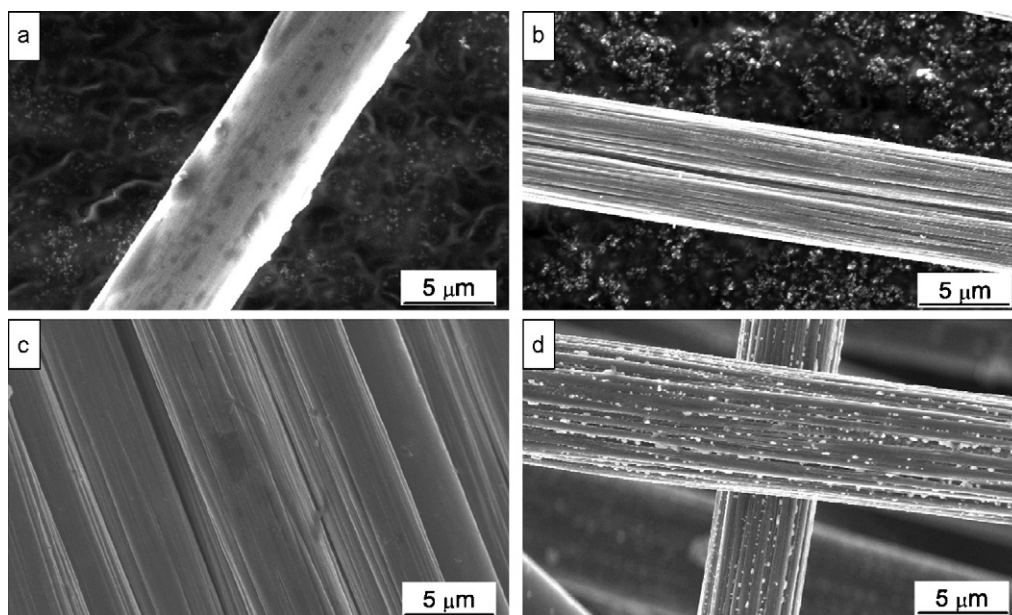
Fig. 3. SEM micrographs of (a) as-received CFs, (b) 200 °C treated CFs, (c) 300 °C treated CFs and (d) 400 °C treated CFs after adsorbing Cu.

Table 1
Surface composition of as-received CFs, 200 °C treated CFs, 300 °C treated CFs and 400 °C treated CFs determined by XPS.

Samples	C 1s (%)	O 1s (%)	O 1s/C 1s (%)
As-received CFs	81.27	18.73	23.05
200 °C treated CFs	83.46	16.54	19.82
300 °C treated CFs	86.94	13.06	15.03
400 °C treated CFs	70.02	29.99	42.83

spectra are C 1s and O 1s peaks. The detailed surface atomic concentrations of as-received CFs, 200 °C treated CFs, 300 °C treated CFs and 400 °C treated CFs by XPS are presented in Table 1. It can be seen clearly that after 400 °C treatment the O 1s concentration dramatically increases, synchronously O 1s/C 1s is up to 42.83%. This indicates the great effect of oxidation treatment on CFs surface.

To better reveal concentrations and types of C–O bonds in surface functional groups of CFs, the C 1s XPS spectra of as-received CFs, 200 °C treated CFs, 300 °C treated CFs and 400 °C treated CFs were deconvoluted into separated peaks (exhibited in Fig. 2). The general trend is that the lower binding energy side loses intensity, while the higher binding energy ones grow. Similar changes in the C 1s spectra were reported for multi-walled nanotubes subjected to oxidation. The assignments of C 1s components to the O-bonding configurations formed in different oxidation temperatures are extremely complicated [18], therefore we carefully assigned the adscription of C 1s. Fig. 2a shows a dominant peak at ∼284.8 eV attributed to C–C component, a peak at ∼286.5 eV stands for phenolic groups [19–23]. After oxidation treatment, a new contribution appears at 289.0 eV (shown in Fig. 2b), which can be assigned to carbon atoms having a total of three bonds to oxygen atoms as present in carboxyl groups (COOH).

Table 2
The calculated percentages of C 1s components.

Samples	C–C (%)	–OH (%)	COOH (%)	–C=O (%)
As-received CFs	51.85	48.15	–	–
200 °C treated CFs	60.26	35.48	4.26	–
300 °C treated CFs	72.09	20.84	7.07	–
400 °C treated CFs	52.78	31.48	5.63	10.10

In Fig. 2d, an additional peak is observed at 287.3 eV, which is attributed to –C=O groups [24]. These bonds and their binding energy, as well as the XPS spectrometer details were compared with the reported literature. Our results are consistent with the publications.

The concentrations of C 1s component are summarized in Table 2. It reveals a decrease in the phenolic groups. While an increase in the sum total of the carbonyl and carboxyl groups, which lead to the broadening of the C 1s towards higher energy (Fig. 2). Similar behavior is also observed in the reported literature. It is well known that oxidized CFs surfaces decompose above 200 °C to produce H_2O [25] and references therein. Water evolves upon dehydration reactions occurring between phenolic groups, carboxyl groups or a hydroxyl function reacting with carboxyl groups. This results in the decrease of phenolic groups on the treated CFs surface, compared to the as-received CFs. The rise in the relative content of carbon bonded to oxygen-containing functions comes mostly from the increases of COOH and –C=O groups, especially –C=O groups (400 °C treatment). To explain the significant increase
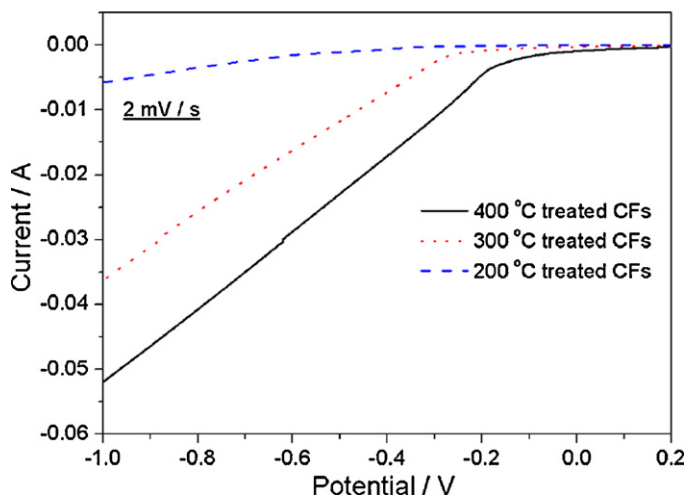

Fig. 4. Current-potential curves for the cathodic process performed from $CuSO_4$ electroplating solution.
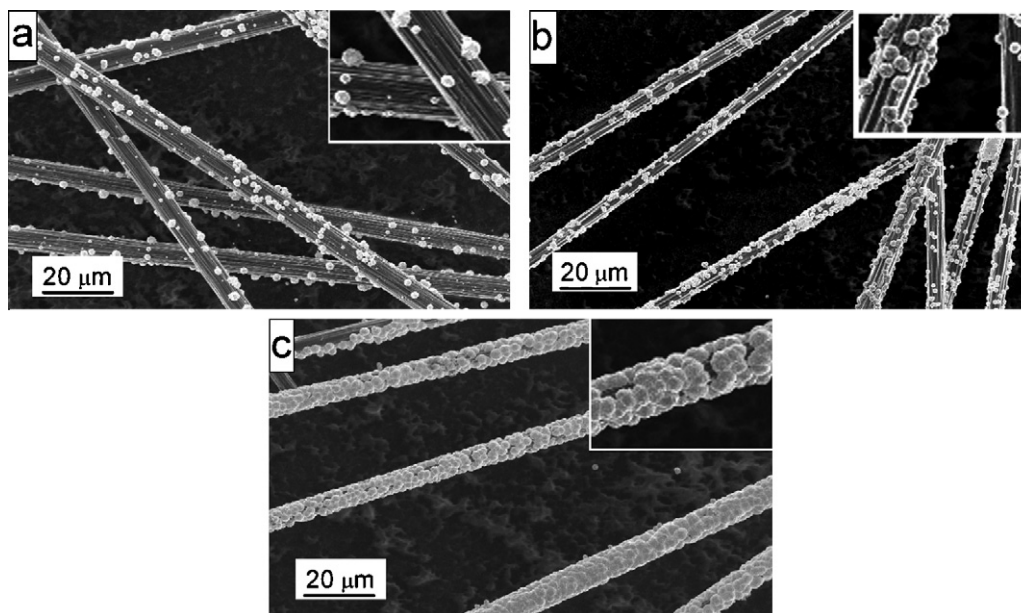
Fig. 5. SEM micrographs of Cu electrodeposition at 0.8 V on (a) 200 °C treated CFs, (c) 300 °C treated CFs and (d) 400 °C treated CFs. Enlarged images are shown in top right corner of each micrograph.

of carbonyl groups in the advanced oxidation stages, A. Barinov et al. [18] propose that the formation of a particular functional group is determined by the distances between the neighboring lower-coordinated 'C defect' atoms. The "C"–"C" distance of the ether-type bonding is short, however it's not easy to form a double atom vacancy for the ether formation, that is, carbonyl formation becomes easily and the content increases.

According to the abovementioned analysis, we draw the conclusions that (i) oxidation treatment can effectively introduce carboxyl and carbonyl groups onto the CFs surface; (ii) after 400 °C oxidation treatment, the concentration of –C=O groups is the highest.

3.2. Effect of functional groups on electrochemical behaviors

In order to eliminate the influence of applied voltage, the blank experiments were carried out in 50 g/L $CuSO_4$ solutions without voltage. The difference in reduction–adsorption capacities of treated CFs is shown in Fig. 3. Copper particles only adsorbed on 400 °C treated CFs (Fig. 3d). From the SEM photographs, it can be clearly observed that copper particles on CFs are very fine. According to Ref. [17,26], the adsorption capacity is influenced by the surface chemical property of CFs. Firstly the adsorption of copper ions is through electrostatic force between Cu^{2+} and oxygen-containing groups on CFs surface, and then the reduction of Cu on CFs happened. Therefore, the creation of Cu crystal nucleus has closely relation to the oxygen-containing group on CFs. As mentioned from XPS results, –C=O groups are present on the 400 °C treated CFs surface and this may indicate that –C=O groups were involved in the reduction reaction of copper.

Electrochemical measurements at pretreated CFs show a range of electrochemical activities based on their surface structure variations. Fig. 4 reports the polarization curves carried out in $CuSO_4$ electroplating solution. It can be seen that the beginning of the plateau of the limiting diffusion current density was shifted to higher electrodeposition overpotentials with the decreasing treatment temperatures. This trend may be ascribed to the effect of effective functional groups on CFs surface. The reduction capacity of 400 °C treated CFs was strongest, results in the needed polarization potential was the lowest.

Based on the above analysis, it can be concluded that Cu electrodeposition on treated CFs involves two stages: the first stage is the reduction–adsorption of Cu due to the functional groups on CFs surface, and the second stage is Cu electrodeposition. Therefore more effective functional groups can improve the reduction capacities of treated CFs and reduce the polarization potential for Cu deposition.

3.3. Effect of functional groups on coating morphology

The morphologies of the copper deposits obtained at 0.8 V in $CuSO_4$ solution are presented in Fig. 5. Small particles (2–3 μm) and a rough surface are observed (Fig. 5a). On the other hand, more small particles are noticeable when the deposition is performed on 300 °C treated CFs (Fig. 5b). Further, small metal particles are relatively uniformly dispersed on the 400 °C treated CFs surface (Fig. 5c). Actually 400 °C treated CFs has more oxygen-containing groups than 200 °C treated CFs or 300 °C treated CFs, thus more copper ions were adsorbed onto the surface of CFs, and more crystal nucleus were created. Under the same action of applied voltage, more copper deposited on the 400 °C treated CFs surface. On the contrary, there are fewer oxygen-containing groups on the surface of 200 °C treated CFs or 300 °C treated CFs, thus there are fewer crystalline center formed on their surface. Therefore, the Cu deposits expand on the totality of the surface after 400 °C treatment because of the highest nuclei population density [15].

4. Conclusions

In this work, the effect of carbon fiber surface treatment on the copper electrodeposition was studied by using XPS, electrochemical technique and SEM. The concentrations and types of oxygen surface functional groups depended on the oxidizing temperature in air. 400 °C treated CFs presented higher amount of surface O-containing groups, especially –C=O groups. The acidic functional groups (i.e. –C=O) on the CFs surface could reduce copper ions from $CuSO_4$ solution, thus it was considered that Cu electrodeposition was the interaction of applied voltage and the reduction of the functional groups on CFs surface. The more functional groups

were, the more Cu deposits were obtained under the same voltage in the electrodeposition process.

Acknowledgements

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