

Short communication

Study on carbon nanotube reinforced phenol formaldehyde resin/graphite composite for bipolar plate

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Abstract

Using carbon nanotubes (CNTs) after different Fenton treatments as a reinforcement and a phenol formaldehyde resin/graphite (PF/G) composite as matrix, a new composite for bipolar plate was formed by hot-pressing. The effects of Fenton, Fenton/ultrasonic and Fenton/ultraviolet treatments on the surface of the CNTs, and the bend strength and conductivity of bipolar plate composite produced using them were investigated. It was found that Fenton/UV treatment was an effective and advanced oxidation process, which could generate a large quantity of hydroxyl groups and few carboxyl groups on the sidewalls of the CNTs, but without severe damage. The functional groups on CNTs after Fenton/ultraviolet treatment can improve the interfacial adhesion between CNTs and matrix, which can improve the bend strength, but does not play an important role in the improvement of the conductivity. The bend strength and conductivity of the composite with 3% CNTs after Fenton/ultraviolet treatment are 68.6 MPa and 145.2 s cm^{-1} , respectively, when pressed at 240°C for 60 min.

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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a very promising power source for residential and mobile applications [1,2]. Bipolar plate is one of the most important components of PEMFC, which accounts for as much as 60–80% of the stack weight [3,4]. Resin/graphite composite is a promising material for bipolar plate due to the advantages of low cost and easy manufacturing [5,6]. Department of Energy (USA) advanced a series of property requirements of resin/graphite composite for bipolar plate, in which the main properties, the conductivity and bend strength were above 100 s cm^{-1} and 25 MPa, respectively [7]. But the resin/graphite composite should have better bend strength and conductivity for commercial applications of PEMFC.

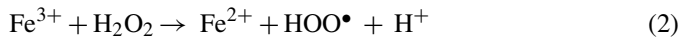
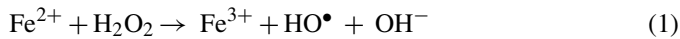
Carbon nanotubes (CNTs) have excellent mechanical and electrical properties [8,9]. So CNTs are used to reinforce phenol formaldehyde resin/graphite (PF/G) composite in our

study. However, the potentials of employing CNTs in composite applications depend strongly on the strong interfacial adhesion between CNTs and matrix. So, surface modification becomes a versatile way to prepare composites with better properties [10,11]. Chemical oxidation treatment of CNTs using high concentration oxidants (such as HNO_3 , $\text{H}_2\text{SO}_4 + \text{HNO}_3$ and KMNO_4) plays an important role in the production of various functional groups and improving its dispersion in the matrix [10,12,13]. However, it is basically a damaging process through the introduction of structural defects along the sidewalls and at the caps of the tubes. It can make the sidewalls of tubes thin, even cut them off, and degrade the original properties of CNTs badly [11].

It is well known that Fenton oxidation reaction, namely the reaction of ferrous ion and hydrogen peroxide ($\text{Fe}^{2+} - \text{H}_2\text{O}_2$), is one of the most powerful advanced oxidation technologies available and can be used in the environmental protection because of the existence of hydroxyl radical (HO^\bullet) generated in the reactions (as shown in the following Eqs. (1) and (2)) in previous studies [14–16]. In our study, CNTs after different Fenton treatments were used to improve the properties of the PF/G composite for bipolar plate. The effects of Fenton, Fenton/ultrasonic

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(US) and Fenton/UV treatment on the surface of the CNTs and properties of the composite were also studied in our work.



2. Experimental

2.1. Materials

Graphite powder was provided by Qingdao Tiansheng Graphite Co. Ltd. (Laixi, PR China); PF resin powder mixed with hexamethylene tetramine was kindly provided by Runda Chemical Industry Co. Ltd. (Laiwu, PR China); CNTs (purity $\geq 95\%$) were kindly provided by Shenzhen Nanoport Company (Shenzhen, PR China); $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and hydrogen peroxide (30% in H_2O) were obtained from Sanhe Regent Co. Ltd. (Yantai, PR China).

2.2. Treatment of CNTs

The procedures of different Fenton treatments were as follows: three glass reaction vessels of 800 ml in volume were used as the reactors for different Fenton treatments. CNTs were added in each vessel at first, then an amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 were added in a stepwise fashion at 30 min intervals in each vessel, in which $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ molar ratio was 1:40, and the pH value was adjusted to 3 ± 0.1 under an acidic condition using 1 M H_2SO_4 . Then different reaction vessels were kept for 3 h in different conditions: Fenton treatment was in static condition without other processes; Fenton/US treatment was carried out in a ultrasonic bath; and Fenton/UV treatment was carried out by some procedures, which include that the CNTs and reactants were stirred by a magnetic stirring apparatus, and the treatment was under the UV lamp, whose power was 20 W and emitting wavelength was 254 nm. Then the CNTs after different treatments were respectively collected on a 200-nm-pore membrane and washed with distilled water until pH value of the filtrate was about 6–7. Finally, the black solid powders were respectively dried in a vacuum chamber at 110°C for 12 h.

2.3. Composite preparation

CNTs, graphite and PF resin powders, in which the content of CNTs was 3% (wt%) and $W_{\text{graphite}}:W_{\text{PF}} = 85:15$, were dry-milled for 60 min in planetary high-energy ball mill (QIF-16) at speed of 300 rpm, and hot-pressing was processed at 240°C in a hot-pressure molding furnace for 60 min to obtain the composite samples. Then the samples were cut into specimens $5\text{ mm} \times 5\text{ mm} \times 20\text{ mm}$ in size for measurement.

2.4. Characterization

Transmission electron microscopy (TEM) images were obtained in JEM-100CxII apparatus and were used to analyze the morphology and size of the CNTs; FTIR spectra were col-

lected using Nicolet Avatar-370 FT-IR spectrophotometer in KBr tablets and were used to analyze the functional groups on the sidewalls of the CNTs. Scanning electron microscopy (SEM) was used to analyze the fracture pattern of composite by using JSM-6380; the conductivity was measured by using apparatus model QJ44; and the bend strength was measured on universal testing machine (CMT5105).

3. Results and discussion

3.1. Effect of different Fenton treatments on the surface of CNTs

It is well known that Fenton treatment is recognized as one of the most powerful advanced oxidation technologies available due to the generation of hydroxyl radical (HO^\bullet), which is one of the most active oxidants except fluorine among all known oxidants. Hydroxyl radical generated in the reaction of hydrogen peroxide and ferrous ion (Eq. (1)) can attack the defect of CNTs by oxidation, which is highly active to bring hydroxyl groups on the sidewalls of CNTs. It can also attack the unsaturated bonds of $\text{C}=\text{C}$ on the sidewalls by electrophilic addition reaction, introducing hydroxyl groups on the sidewalls of CNTs [17,18]. However, hydroxyl groups are unstable to be oxidized to carboxyl groups due to the further oxidization of hydroxyl radical. The mechanism of oxidizing reaction of carbon nanotubes is shown in Fig. 1.

The FTIR spectra of CNTs before and after different Fenton treatments are shown in Fig. 2. There were no significant functional groups detected on the pristine CNTs (Fig. 2(a)). Fig. 2(b) presents the FTIR spectra of CNTs after Fenton treatment, whose peaks at 1050–1150, 1580, 1650 and $3000\text{--}3600\text{ cm}^{-1}$ start appearing. FTIR spectra of the CNTs after Fenton/US treatment are shown in Fig. 2(c). Compared with Fig. 2(b), we discover that Fig. 2(c) is highly similar to Fig. 2(b), which indicates that the application of US technology cannot improve the treating effect of CNTs. The FTIR spectra of CNTs after Fenton/UV treatment are shown in Fig. 2(d). Compared with that after above two treatments, there appear some changes: it can be found that a new peak appeared at 1715 cm^{-1} , and a typically broad and obtuse peak appeared at $3000\text{--}3600\text{ cm}^{-1}$. The vibrational band assignments are presented in Table 1 [19,20], indicating that hydroxyl groups were brought in all the treatments, and few carboxyl groups were brought in the Fenton/UV treatment.

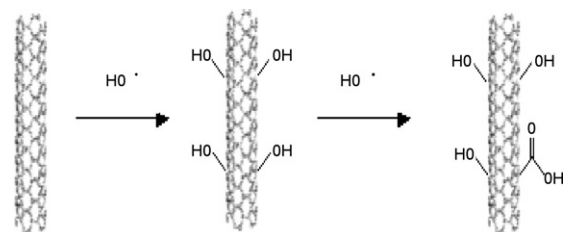


Fig. 1. Mechanism of oxidized reaction of carbon nanotubes.

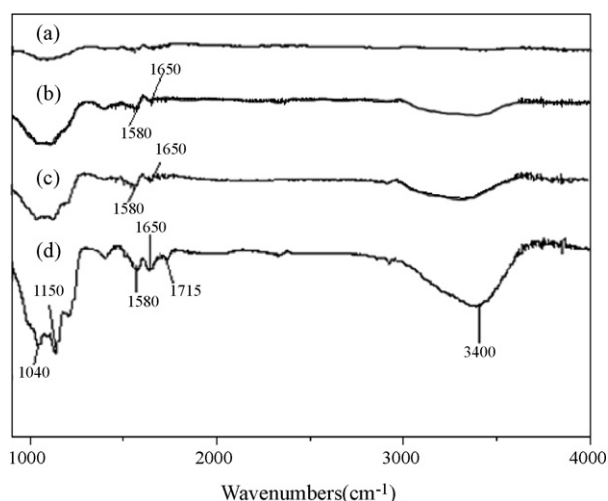
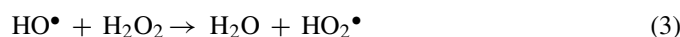


Fig. 2. FTIR spectra of (a) pristinine, (b) Fenton reagent oxidized, (c) Fenton/US oxidized and (d) Fenton/UV oxidized carbon nanotubes.

Table 1
Assignment of peaks in the IR spectrum of different oxidized carbon nanotubes

Vibrational band (cm ⁻¹)	Assignment
1050–1150	C–O str in hydroxyl groups
1580	–C=C– str
1650	C=O str in quinone groups
1715	C=O str in carboxyl groups
3000–3600	OH str in hydroxyl groups and carboxyl groups

Hydroxyl radical generated in the Fenton reaction may be consumed at high hydrogen peroxide concentrations (shown in the Eq. (3)) [21]. However, HO₂•, compared with hydroxyl radical, does not play an important role in the oxidizing processes due to its low reactivity. So, Fenton treatment generates small quantity of hydroxyl groups (shown in Fig. 2(b)). The *hν* provided by US and UV technology may accelerate the generation of hydroxyl radical (shown in the Eqs. (4) and (5)) [22]. The application of US technology provides so low *hν* that Fenton/US treatment cannot generate more hydroxyl radical to improve the treating effect of CNTs (shown in Fig. 2(c)). But the UV technology can provide higher *hν* to accelerate the generation of hydroxyl radicals, which can accelerate oxidized processes, then generate a large quantity of hydroxyl groups and few carboxyl groups (shown in Fig. 2(d)):



The TEM images of purified and Fenton/UV oxidized CNTs are shown in Fig. 3. It is seen from the images that the diameter of CNTs increases slightly. It indicates that there is some matter on the sidewalls of CNTs, which may be functional groups and some impurities (such as iron compound). Synchronously, the slight variation of diameter indicates Fenton/UV treatment cannot make the sidewalls of tubes this obviously, and may not degrade the original properties of nanotubes badly. So, the



Fig. 3. TEM image of different CNTs (a) pristinine CNTs and (b) CNTs after Fenton/UV treatment.

primary mechanism of Fenton reagent treating CNTs is that hydroxyl radical generated in the Fenton reaction can attack the unsaturated bonds of C=C on the sidewalls by electrophilic addition reaction, introducing functional groups on the sidewalls of CNTs, not that it brings hydroxyl groups on the sidewalls of CNTs by oxidation.

3.2. Effect of different Fenton treatments on the properties of the PF/G composite

Table 2 shows the bend strength and conductivity of different composites. It indicates that the addition of CNTs after Fenton or Fenton/US treatment reduces the bend strength and conductivity, and cannot reinforce the properties of the PF/G composite; the addition of CNTs after Fenton/UV treatment can improve the bend strength of composite, but does not play an important role in the improvement of the conductivity.

Table 2
Properties of investigated materials

System	Bend strength (MPa)	Conductivity (s cm ⁻¹)
PF/G	61.6	141.6
3% Fenton oxidized CNTs–PF/G	58.2	110.2
3% Fenton/US oxidized CNTs–PF/G	58.7	121.3
3% Fenton/UV oxidized CNTs–PF/G	68.6	145.2

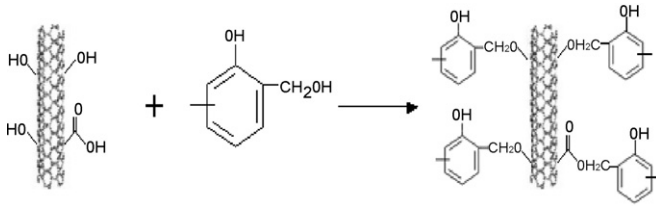


Fig. 4. Chemical reaction between treated CNTs and PF resin.

The interfacial adhesion between CNTs and matrix plays an important role in improving the properties of the PF/G composite. So the interfacial adhesion between CNTs and PF resin (the binder in composite) is crucial for improving the properties. The treated CNTs are expected to have a chemical reaction with PF resin (shown in Fig. 4). It indicates that the interface between CNTs and PF resin depends on the quantity of groups on the CNTs.

The CNTs after Fenton or Fenton/US treatment have a little quantity of hydroxyl groups (shown in Fig. 2(b and c)). So, the interfacial adhesion between CNTs and PF resin is weak, which lead to the generation of void around the interface. It can reduce density of composite, then reduce the properties of the PF/G composite [23]. The CNTs after Fenton/UV treatment have a large quantity of hydroxyl groups and few carboxyl groups (shown in Fig. 2(d)), which can bond the interface better, and generate little void around the interface. PF resin bonded with CNTs can have a polyreaction with others, which can increase the diameter of CNTs observably (shown in Fig. 5).

The bend strength is improved obviously due to the excellent mechanical property of CNTs. The bend strength of the PF/G composite was reinforced by about 11.6% as the concentration of Fenton/UV treated CNTs is 3%. But the conductivity cannot be reinforced obviously from Table 1. On the one hand, CNTs have excellent electrical property. On the other hand, the π electron on the sidewalls of CNTs can be bounded due to the addition of functional groups, which can increase the steric hindrance

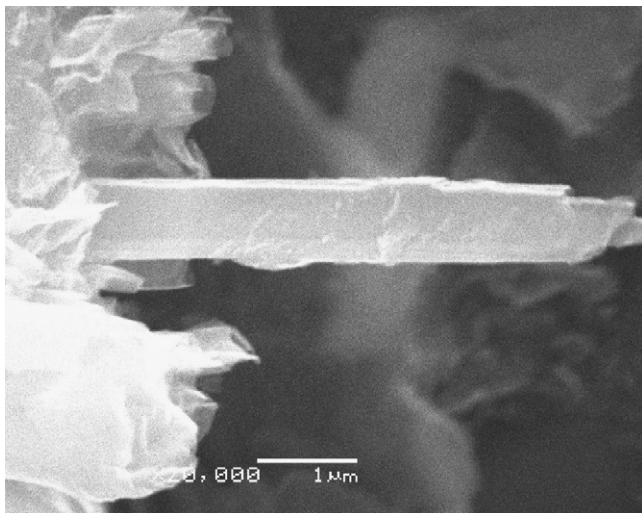


Fig. 5. SEM image of 3% Fenton/UV oxidized CNTs–PF/G composite.

and reduce the electrical property of the composite [24]. So, the electrical conductivity can only be reinforced slightly due to the combined action of two reasons.

4. Conclusions

This work reports the successful use of Fenton/UV treatment on CNT reinforced PF/G materials, which can improve the bend strength of the PF/G composite efficiently.

Fenton or Fenton/US treatment can generate a little quantity of hydroxyl groups on the sidewalls of CNTs. After these treatments CNTs reduce the bend strength and conductivity of the PF/G materials. Fenton/UV treatment can generate a large quantity of hydroxyl groups and few carboxyl groups on the sidewalls of CNTs, but without severe damage. The surface functional groups of CNTs after Fenton/UV treatment can improve the interfacial adhesion between CNTs and matrix. The addition of CNTs after Fenton/UV treatment can improve the bend strength of the PF/G composite efficiently. The primary mechanism of Fenton reagent treating CNTs is that hydroxyl radical generated in the Fenton reaction can attack the unsaturated bonds of C=C on the sidewalls by electrophilic addition reaction, introducing hydroxyl groups on the sidewalls of CNTs.

The bend strength and conductivity of composite with 3% CNTs after Fenton/UV treatment are 68.6 MPa and 145.2 s cm^{-1} , respectively, pressed at 240°C for 60 min, which can meet the requirements of the bend strength and conductivity of resin/graphite composite for bipolar plate.

Acknowledgement

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