One-step fabrication of carbon fiber derived from waste paper and its application for catalyzing tri-iodide reduction

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Abstract. Two carbon fibers were first fabricated by one-step pyrolysis of papers (filter paper and facial tissue), and then employed as catalytic materials for counter electrodes in dye-sensitized solar cells (DSCs) to investigate their potential application. The results show that the microstructure transformation and main weight loss of both the papers are mainly happened in the temperature range of 300–400 °C. After pyrolysis at 800 °C, the weight remaining of the filter paper and facial tissue is 1.92% and 4.95%, respectively. The obtained carbon fibers belong to an amorphous carbon consisting of the randomly oriented stacks of graphene sheets. The diameters of both the carbon fibers are about 10 μm, on which there are a certain amount of fine carbon nanofibers. The amorphous microstructure and unique fine nanofibers of the carbon fibers induce more excellent catalytic activity for triiodide ion reduction compared with the biochar (derived from poplar leaf) and the graphite. As a result, the carbon fiber based DSCs display obviously higher efficiency than the biochar or graphite based ones. The conversion efficiency of the DSCs employing the filter paper derived carbon fiber, facial tissue derived carbon fiber, biochar and graphite is 4.72%, 4.70%, 1.33% and 0.77%, respectively.

1. Introduction

Waste papers, common renewable resource, have been traditionally recycled in paper industry as fibrous raw materials [1]. Moreover, waste papers have often been employed to prepare carbon fibers with high-added-value owing to their low ash content and reasonable carbon residue, which have been applied in several fields, such as gas adsorption [2] and reaction formation of SiC ceramics [3]. The invention of dye-sensitized solar cells (DSCs) opens a potential gate for the application of the waste papers derived carbon fibers in new energy field.

As a kind of devices to harness the limitless power of the Sun, DSCs have attracted increasing interest for their low cost, easy fabrication, flexibility and moderate efficiency [4]. Typically, a DSC consists of a dye sensitiser, TiO2 photoanode, an electrolyte and a Pt counter electrode. The role of the Pt counter electrode, which consists of Pt film deposited on FTO glass, is to collect electrons arriving from the external circuit and to catalyze the reduction of triiodide ion. However, the scarce resource, high costs and poor stability of Pt could inhibit its large-scale application in the future [5]. To solve this problem, several carbon materials, such as carbon black, graphite, activated carbon, mesoporous carbon, carbon nanotubes and graphene, have been used as catalysts to replace Pt for counter electrode, and their devices show favorable photovoltaic performances [6-8]. Compared with the above carbon materials, the carbon fiber obtained from one-step pyrolysis of waste paper shows simpler process, more abundant raw materials and more environmental friendly. Therefore, to introduce the waste paper based carbon fiber into the DSCs as the counter electrode not only reaches the destination on its...
application in new energy field, but also displays a potential way with low-cost to replace the Pt counter electrode.

In this research two kinds of carbon fibers were first fabricated by one-step pyrolysis of waste papers including filter paper and facial tissue, and then used as catalytic materials for counter electrodes in DSCs to investigate their potential application. Both of the carbon fiber based devices show more excellent photovoltaic performances than the biochar or graphite based ones. The conversion efficiency of the DSCs employing carbon fiber electrodes is around 4.70% while that of the devices consisting of biochar and graphite electrodes is no more than 1.40%.

2. Experimental

2.1. Fabrication and characterizations of carbon fiber

Two papers were individually selected as the precursors to prepare the carbon fibers. The paper was pyrolyzed by slowly heating to 800 °C for 1h in flowing N2 atmosphere, and mechanically milled to obtain carbon fiber powders. The carbon fibers derived from filter paper and facial tissue are labeled as CF-FP and CF-FT, respectively.

Thermal decomposition behavior of the papers was examined by a simultaneous thermogravimetry−differential thermal analysis (TG−DTA; SDT-Q600, TA, USA) using a heating rate of 10 °C·min⁻¹ in N2. The crystal microstructure of the carbon fibers was identified by an X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany) using Cu Kα radiation with a wavelength (λ) of 0.154056 nm. The scanning step was 0.02 °, and the scanning area was 15–75°. The morphology of the carbon fibers was characterized by a field emission scanning electron microscopy (FE-SEM; JSM-6701F, JEOL, Japan). N2 adsorption-desorption isotherms of the carbon fibers were examined on an automatic adsorption instrument (ASAP 2020M, Micromeritics, USA), using nitrogen at 77 K. Surface areas were calculated by Brunner−Emmet−Teller (BET) method from N2 desorption isotherms.

2.2. Configuration and measurements of carbon fiber based cells

The DSC was configured by assembling a N719 sensitized TiO2 photoanode and a carbon fiber counter electrode, between which was separated by using a 50 μm thick spacer. The surface area of both TiO2 film and carbon fiber film was about 0.7 cm × 0.7 cm. For obtaining the photoanode, a transparent TiO2 film was first coated on the FTO substrate, and then a second layer containing light scattering particles of TiO2 was coated on the obtained TiO2 film. After sintered at 450 °C for 30 min, the double-coated TiO2 film was further treated with TiCl4 aqueous solution followed by heat treatment at 450 °C for 30 min. The photoanode was obtained by further immersing the double-coated TiO2 film into a N719 ethanol solution at room temperature for 24 h [9]. The electrolyte was 0.5M LiI, 0.05M I2, 0.5M TBP in a solvent of 3-methoxypropionitrile. The carbon fiber electrode was prepared by coating a carbon fiber blended paste on FTO substrate and then heated at 120 °C for 2h. The carbon fiber blended paste was obtained through grinding 200mg carbon fiber powders, 20mg carboxymethyl cellulose (CMC) and 5ml ethylalcohol aqueous solution.

Electrochemical impedance spectroscopy (EIS) measurements were conducted with an electrochemical workstation(CS310, Corrtest, China) at 10 mV of amplitude. A symmetric cell consisting of two identical counter electrodes and an electrolyte was used in the EIS measurements. The electrolyte was the same as the one used in the fully functional DSCs. Cyclic voltammetry (CV) experiments were performed using a conventional three-electrode system at a scan rate of 50 mV·s⁻¹. The as-prepared electrode, Pt coil, and Pt wire were used as the working electrode, auxiliary electrode, and reference electrode, respectively. The electrolyte was an acetonitrile solution containing 0.1 M LiClO4 as the supporting electrolyte and 10 mM LiI+ 1 mM of I2 as the redox couple. Photocurrent-voltage performances of the DSCs were measured under the illumination of a Xenon light source. The light intensity was 100 mW·cm⁻².
3. Results and discussion
To explore the thermal decomposition behavior of the filter paper and facial tissue selected for the preparation of the carbon fibers, their TG and DTA curves were obtained, as shown in Figure 1. It is obvious that both the TG curves are similar. There are obvious weight losses in the temperature ranges of 20–80 °C and 300–400 °C in both the curves. The weight loss in the first temperature range, which is mainly caused by the evaporation of adsorbed water, is 4.57% and 5.36% for the filter paper and facial tissue, respectively. The weight loss in the second temperature range is more serious than that in the first temperature. In this temperature range (300–400 °C), the weight loss of the filter paper is 88.31% while that of the facial tissue is 78.87%. The occurrence of an endothermic peak in the DTA curves of both the papers is accompanied by the serious weight loss. The above results suggest that the microstructure in both the paper is mainly changed in the temperature range of 300–400 °C. Moreover, with increasing temperature to 800°C, the weight loss of both the papers reaches a plateau. The weight remaining of the filter paper and facial tissue at 800°C is 1.92% and 4.95%, respectively.

The XRD patterns of the carbon fibers are demonstrated in Figure 2(a). No obvious difference can be observed between the patterns of CF-FP and CF-FT, meaning the existence of nearly identical microstructure in both the carbon fibers. Two broadening peaks of (002) and (100) associated with graphite characteristic appear in the patterns. According to Bragg formula \(d = \frac{\lambda}{2\sin \theta}\), the layer distance of the (002) crystal plane \(d_{(002)}\) of the carbon fibers is estimated to be about 0.3890 nm, which is larger than that of the (002) crystal plane of the graphite (0.3335 nm). It is reasonable to conclude that both of the carbon fibers prepared from the pyrolysis of the papers belong to an amorphous carbon consisting of the randomly oriented stacks of graphene sheets. The amorphous microstructure in the carbon fibers is beneficial for catalyzing the reduction of triiodide ion since the active sites in the carbon materials for catalysis are located at the edges of graphene stacks [10].

![Figure 1. TG (a) and DTA (b) curves of different papers used for the preparation of carbon fibers.](image)

The SEM morphologies of the carbon fibers of CF-FP and CF-FT are illustrated in Figure 3. It is obvious from Figure 3 (a) and (b) that both the carbon fibers show different stack patterns. The carbon fibers in CF-FP derived from filter paper connect each other as a net. In contrast, the carbon fibers in CF-FT derived from facial tissue have oriented distribution with regular wave-structure in the oriented direction. The diameters of the carbon fibers in CF-FP and CF-FT are about 10 μm. The amplified SEM images in Figure 3(c) and (d) further demonstrate that there are a certain amount of fine carbon nanofibers on the surfaces of the 10 μm-sized carbon fibers in CF-FP and CF-FT. The fine nanofibers enlarge the surface areas of the samples, resulting in the increase of the active sites for catalysis. The \(N_2\) adsorption-desorption isotherms of the carbon fibers are displayed in Figure 2(b). It is obvious that both of the carbon fibers exhibit type II isotherms, which are mainly induced by adsorption-desorption of macroporous or dense materials [11]. The inflection point in the isotherms, as indicated by the
arrow, is a cut-off point of the adsorptions of monolayer and multilayer. The above results indicate that the single carbon fiber belongs to dense materials, which limits the surface areas of CF-FP and CF-FT to a certain degree. The value of BET surface area ($S_{\text{BET}}$) of CF-FP and CF-FT is 2.21 and 3.24 m$^2\cdot$g$^{-1}$, respectively.

**Figure 2.** XRD patterns (a) and N$_2$ adsorption-desorption isotherms (b) of carbon fibers derived from different papers.

**Figure 3.** SEM morphologies of carbon fibers derived from different papers. (a) and (c) CF-FP from filter paper; (b) and (d) CF-FT from facial tissue.
To insight into the catalytic activities of the carbon fibers derived from the papers, the EIS and CV were employed. The typical Nyquist plots for the carbon fiber counter electrodes are shown in Figure 4(a). For comparison, Figure 4(a) also illustrates the Nyquist plots of biochar and graphite counter electrodes, which were respectively prepared by coating a biochar (derived from poplar leaf) blended paste and a graphite blended paste on the FTO substrates and then annealing at 120 °C for 2h. Two impedance parameters, charge transfer resistance ($R_{ct}$) and ohmic serial resistance ($R_s$), can be achieved from plot fitting by using the equivalent circuit, and are summarized in Table 1. The $R_{ct}$ characterizes the catalytic activity for the triiodide reduction, and the $R_s$ is mainly related to the sheet resistance of the electrode [12]. Both of the carbon fiber electrodes present lower $R_{ct}$ than the biochar and graphite electrodes, implying higher catalytic activity toward the triiodide ion reduction. The $R_{ct}$ values of the carbon fiber electrodes from CF-FP and CF-FT are respectively 4.42 and 4.15 Ω cm$^2$ while those of the biochar and graphite electrodes are respectively 12.50 and 52.50 Ω cm$^2$. The more excellent catalytic activity of the carbon fibers could be mainly attributed to their amorphous microstructure and unique fine nanofibers (Figure 2 and 3). Moreover, the almost identical $R_{ct}$ values between the carbon fiber electrodes suggest nearly same catalytic activity toward the triiodide ion reduction. Figure 4(a) also shows that the sheet resistance of each carbon fiber electrode is lower than that of the biochar or graphite electrode. The $R_s$ values of the electrodes prepared from CF-FP, CF-FT, biochar and graphite are 22.61, 23.38, 38.60 and 46.15 Ω cm$^2$, respectively.

![Figure 4](image_url)

**Figure 4.** Nyquist plots (a) and CVs (b) of counter electrodes prepared from various carbon materials. The insert in (a) shows the expanded range in high frequency region.

**Table 1.** Electrochemical performances of counter electrodes obtained from various carbon materials and their photovoltaic properties for DSCs*

| Carbon      | Electrochemical | Photovoltaic |
|-------------|-----------------|--------------|
|             | $R_{ct}$/Ω cm$^2$ | $R_s$/Ω cm$^2$ | $E_p$/V | $J_{sc}$/mA·cm$^2$ | $V_{oc}$/V | $FF$ | $\eta$/% |
| CF-FP       | 4.42            | 22.61        | 0.45   | 15.02          | 0.697      | 0.451 | 4.72      |
| CF-FT       | 4.15            | 23.38        | —      | 14.80          | 0.686      | 0.463 | 4.70      |
| Biochar     | 12.50           | 38.60        | —      | 10.96          | 0.488      | 0.249 | 1.33      |
| Graphite    | 52.20           | 46.15        | 0.67   | 9.90           | 0.447      | 0.175 | 0.77      |

*R$_{ct}$: Charge transfer resistance; $R_s$: Ohmic serial resistance; $E_p$: Peak separation between the $P_{ox}$ and $P_{red}$; $J_{sc}$: Short-circuit current density; $V_{oc}$: Open-circuit voltage; $FF$: Fill factor; $\eta$: Conversion efficiency.
The CVs for the carbon fiber (CF-FP) and graphite electrodes are displayed in Figure 4(b). A pair of redox peaks are observed in both the CV curves. The peak in the positive side is attributed to the oxidation reaction, while the negative one results from the reduction reaction [13]. In the reduction peak \( P_{\text{red}} \), the current density of the carbon fiber electrode is higher than that of the graphite electrode. It means that there are a faster reaction rate and a higher catalytic activity for the triiodide ion reduction on the carbon fiber electrode than on the graphite electrode [14]. Moreover, the reduction peak for the carbon fiber electrode shifts more positively compared with the graphite electrode, indicating that the reduction reaction takes place at lower overpotential on the former electrode than on the latter electrode [15]. In the oxidation peak \( P_{\text{ox}} \), the carbon fiber electrode presents lower current density compared with the graphite electrode, which is believed to have an insignificant effect on the catalytic performances [16]. The peak separation \( E_p \) between the \( P_{\text{ox}} \) and \( P_{\text{red}} \) is another important parameter to estimate the catalytic properties [17]. For clarity, the \( E_p \) is listed in Table 1. The higher catalytic activity of the carbon fiber electrode is found to be in consistency with its respective lower \( E_p \) of 0.45 V, with reference to that of the graphite electrode (0.67 V). Evidently, the above results are consistent with the EIS analysis (Figure 4a).

Figure 5 shows the photocurrent density–voltage \( (J-V) \) curves of the DSCs employing four kinds of carbon materials as counter electrodes: CF-FP, CF-FT, biochar and graphite. The parameters of the photovoltaic properties are summarized in Table 1. The conversion efficiency \( \eta \) of the DSCs employing the carbon fiber electrodes from CF-FP and CF-FT is respectively 4.72% and 4.70%, which are evidently higher than that of the devices with the biochar and graphite electrodes. The \( \eta \) value of the biochar and graphite based cells is respectively 1.33% and 0.77%. Compared with the biochar and graphite electrodes, the most pronounced change by using the carbon fiber electrodes is the rapid increase of the Fill factor \( (FF) \) of the devices. The \( FF \) values of the DSCs consisting of the electrodes from CF-FP, CF-FT, biochar and graphite are 0.451, 0.463, 0.249 and 0.175, respectively. The outstanding catalytic activity of the carbon fiber electrodes is a key factor to enhance the \( FF \) and \( \eta \) of the devices.

![Figure 5. J–V curves of DSCs consisting of counter electrodes based on various carbon materials.](image)

4. Conclusion
During pyrolysis, the microstructure transformation and main weight loss of the selected papers are mainly emerged in the temperature range of 300–400 °C. The weight remaining of the filter paper and facial tissue at 800°C is 1.92% and 4.95%, respectively. The obtained carbon fibers belong to an amorphous carbon consisting of the randomly oriented stacks of graphene sheets. The diameters of both the carbon fibers are about 10 μm, on which there are a certain amount of fine carbon nanofibers. When both of the carbon fibers are employed as the catalytic materials for the counter electrodes, the corresponding DSCs display obviously higher efficiency than the devices based on the biochar and...
graphite as counter electrodes. The conversion efficiency of the DSCs employing the filter paper derived carbon fiber, facial tissue derived carbon fiber, biochar and graphite is 4.72%, 4.70%, 1.33% and 0.77%, respectively. The high efficiency is mainly attributed to the unique structural and morphological characteristics of the carbon fibers, such as amorphous microstructure and unique fine nanofibers. Moreover, the low temperature (120 °C) treatment process can be employed to fabricate a low-cost and efficient counter electrode for both glass based DSCs and flexible DSCs.

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