Tobacco Waste Biomass for Electrochemical Energy Storage Application

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Abstract. A large amount of industrial and agricultural wastes are generated in the tobacco industry, such as tobacco stems, tobacco stalks, and tobacco leaves. How to increase the economic added value of industrial and agricultural wastes is an important issue. It is a promising value-added way that these biological wastes are recycled into carbon materials with excellent electrochemical properties. Herein, biochar were prepared from tobacco waste biomass (mainly tobacco stems, tobacco stalks and tobacco leaves) through one-step carbonization. The as-obtained biochar exhibited high specific capacitance of 305.92 F·g⁻¹ (tobacco stems), 328.07 F·g⁻¹ (tobacco stalks), and 272.48 F·g⁻¹ (tobacco leaves) at 1 A·g⁻¹, when tested in a three-electrode system with 6 M KOH electrolyte. This study highlights the possibility of reusing tobacco waste to produce low-cost, green and high-performance carbon-based electrode materials for sustainable electrochemical energy storage systems.

1. Introduction

In recent years, the production of biomass carbon materials from agricultural wastes has become a research hotspot in energy and the environment. Biochar is widely used in various fields because of its advantages of low cost, wide sources, and diversified morphology, which has considerable economic value. Biomass has become an ideal precursor for preparing various types of carbon materials because of its abundant reserves, convenient transportation and sustainable development [1], [2]. There have been many reports on the use of biological waste to prepare biochar, such as banana peels [3], corn cobs [4], baobab husks [5], pomegranate peels [6] and so on. The carbon-based materials were prepared with biological waste by physical, chemical activation and other methods, which can be used as electrode materials for supercapacitors. This has far-reaching significance for improving the economic value of biological waste and reducing the environmental pollution.

China is the largest producer of tobacco in the world. A large amount of tobacco waste is generated every year in the process of tobacco production and processing. According to the China Statistical Yearbook (2015), the tobacco planting area was 1.60×10⁶ hm² in 2015, producing tobacco leaves 2.20×10⁶ tons and about 1.20×10⁶ tons of tobacco stems waste were generated at the same time [7]. It is difficult to use these tobacco wastes as fuel alone due to the high potassium content and low calorific value. Tobacco wastes are treated as waste or incinerated directly, which will cause the...
environment polluted seriously and the resources wasted seriously. If these tobacco wastes are recycled, it will bring huge economic benefits, good social benefits and ecological benefits [8].

To make full use of resources and develop sustainable energy, it is very promising to convert biomass waste into high value-added and high-performance carbon materials by simple processes. Herein, waste tobacco stems, tobacco stalks, and tobacco leaves form tobacco industry were used as precursors to prepare biochar by directly carbonized, which were used as electrode materials for supercapacitor. And these carbon materials showed higher mass specific capacitance and good rate performance and stability.

2. Experimental Details

The preparation of biochar: The tobacco waste biomass (mainly tobacco stems, tobacco stalks and tobacco leaves) were used to prepare biochar through one-step carbonization. The tobacco waste biomass were first cut into small pieces, washed several times thoroughly with deionized water, absolute ethanol and dried in an oven at 80 °C overnight. Then, the cleaned tobacco stems, tobacco stalks and tobacco leaves were pyrolyzed in a tube furnace at 800 °C at a heating rate of 5 °C·min-1 under nitrogen flow for 2 h. After cooling to room temperature, the biochar was washed several times with 1 M HCl and deionized water until a natural pH value was achieved. Finally, the as-prepared biochar powder was dried at 80 °C overnight, which was used for electrode materials of supercapacitors.

Preparation and electrochemical measurement of electrode carbon: The electrodes were prepared as follows. The obtained carbon, conductive agent (acetylene black), and PTFE (poly tetra fluoroethylene) were mixed with ethanol in the mass ratio of 8:1:1. The slurry was pasted uniformly on the nickel foam current collectors (1 cm2) and dried in an oven at 80 °C overnight. The electrochemical measurements were performed on the CHI760 electrochemical workstation (Chenhua, Shanghai, China). For a three-electrode system, platinum foil (1 cm2) and Hg/HgO electrode were utilized as the counter and reference electrodes, respectively.

3. Results and Discussion

3.1. SEM Analysis

The microstructures and the morphologies of the as-prepared biochar were characterized by SEM. Fig. 1 (a)-(c) are the SEM microscopic characterization images of the biomass carbon materials derived from tobacco stems, tobacco stalks, and tobacco leaves by directly carbonized. As shown in Fig. 1, all the samples exhibited a porous structure after being carbonized at a high temperature. Among them, the porous structure of as-obtained biochar of tobacco leaves by carbonization was particularly obvious, which may be related to their own natural pore structure. The porous carbon materials provided a short diffusion distance to the inner surface by acting as an ion buffer reservoir. The microporous core extended into the particles, when they were immersed in the electrolyte [9]. Therefore, this porous structure promotes ion transport by forming channels, which provide low ion transport resistance.
For further characterization, XRD tests were performed on three biomass carbon samples. As shown in Fig. 2, all samples have a strong peak at 25°, corresponding to the (002) crystal plane of the graphite structure; and a weaker biological diffraction peak at 43°, corresponding to the (100) crystal plane of the graphite structure, which shows that the obtained biochar has a fixed structure [10]. According to the strong peaks of the samples in the low-angle region of XRD, it reflects that the prepared biochar has a large number of microporosity structures. Thus, it has high specific surface area and excellent electrochemical performance.
3.2. Electrochemical Characterization
The electrochemical performances of the obtained biochar were tested in a three-electrode system (Fig. 3). All the CV curves of the samples (Fig. 3 (a)) retained a roughly rectangular-like shape without any pronounced redox peak at 10 mV·s⁻¹, supporting the rate of feature and good charge-discharge performance of the biochar-based electrode. And this is consistent with the characteristics of electric double-layer capacitance. As shown in Fig. 3 (b), the GCD curves of the samples at 1 A·g⁻¹ are involved in a highly symmetrical and linear isosceles triangle shape, which confirms the superior reversibility of the prepared electrodes during the working process. Moreover, the gravimetric specific capacitances of the samples were also calculated at different current densities (Fig. 3 (c)). The specific capacitances are 266.73 F·g⁻¹ (tobacco stem), 288.75 F·g⁻¹ (tobacco stalk) and 247.53 F·g⁻¹ (tobacco leaf) at 1 A·g⁻¹ current density, respectively. At 10 A·g⁻¹ current density, the specific capacitance of samples can still reach 213.75 F·g⁻¹, 215.03 F·g⁻¹, and 198.39 F·g⁻¹, respectively, which showing good rate performance. The outstanding capability was mainly due to the hierarchical porous structures, which could serve as both electrolyte reservoirs and short ion channels for ion transfers [11]. This is consistent with its SEM images. Fig. 3 (d) shows the Nyquist plots of the samples composed of two regions: one was a semicircle at high frequency; this semicircle corresponds to the reaction resistance produced by the reaction of the ions in the electrolyte with functional groups of the electrode surface. Another was a straight line at low frequency, demonstrating their ideal polarizable electrode characteristic and rapid electron mobility [12]. In addition, as shown in the EIS diagram, the curves of all samples are almost parallel to the Y-axis, indicating that the internal resistance of the samples is very small. These results also show that the prepared carbon materials are multi-spaced and the distribution of different pore diameters (as shown in Figure 1) can provide fast electron and ion transmission channels.
Figure 3. The electrochemical test curve of tobacco stem, tobacco stalk and tobacco leaf (a) CV (10 mv·s⁻¹) (b) GCD (1 A·g⁻¹) (c) capacitance retention rate (d) Nyquist plot

4. Summary
In conclusion, a biochar material was successfully prepared from tobacco waste biomass by direct carbonization, which provided a green and simple method for the resource utilization of tobacco waste biomass. Experiment results confirmed that the as-prepared carbon materials based electrodes achieved high specific capacitances of 305.92 F·g⁻¹ (tobacco stems), 328.07 F·g⁻¹ (tobacco stalks), and 272.48 F·g⁻¹ (tobacco leaves) at 1 A·g⁻¹ current density and maintained about 80%, 74%, and 80% of the initial capacitance retention after the current density was changed from 1 to 10 A·g⁻¹, respectively. These findings highlight the possibility of using tobacco waste biomass to produce green, low cost and high performance carbon-based electrode materials in electrochemical energy storage systems. Moreover, the method of this study is also applicable to the recycling and utilization of other bio-waste resources.

5. Acknowledgement
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6. References

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