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Carbonized *Enteromorpha prolifera* with porous architecture and its polyaniline composites as high-performance electrode materials for supercapacitors

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ABSTRACT

Hierarchical three-dimensional porous carbon has been prepared through facile and moderate carbonization of *Enteromorpha prolifera*, a sustainable biomass-based carbon source. The novel carbonization process retains the original algae cell morphology with unusual egg-shell-like structure and develops porosity. Both the *Enteromorpha prolifera* derived porous carbon and its polyaniline (PANI) composites, synthesized by rapid in-situ electrochemical deposition, have been fabricated into supercapacitor electrodes. Both the electrodes exhibit distinguished and long-lasting capacitance. The porous carbon and PANI composite electrode realizes initial capacitance of 622 F g^{-1}, 3 times that of *Enteromorpha prolifera* derived carbon electrode (180 F g^{-1}), and remains 87% capacitance retention rate after 2000 charge/discharge cycles at 1 A g^{-1} current density. The investigation demonstrates the great potential of high-performance carbon composite materials and whose energy storage device may be derived from *Enteromorpha prolifera*, a biomass-based sustainable carbon source as a result of a sea waste invoking great environment concerns.

1. Introduction

Carbon materials are the mostly widely used electrode materials due to their chemical corrosion resistance, large surface area, desirable electrical properties and moderate cost [1–3]. In particular, porous carbon materials receive increasingly wide deployment as electrode materials in energy devices, spanning from dye sensitized solar cell [4,5] and fuel cell [6–9] to Li secondary battery [10–12] and supercapacitor [13–28]. Graphite, petroleum, coal or products derived from them were the main raw materials for traditional carbon electrode, which are non-renewable resources that we will lose forever once we consume them. With the environmental deterioration and an exacerbation of the global energy crisis, development of simple low-cost strategies is still a foremost challenge for synthesis of nanostructured carbon materials. As a result, people are focusing on carbon precursor derived from biomass, the advantage of which is that they can continually reproduce under natural or artificial maintenance. Natural biomass-based organic materials, which are present ubiquitously on earth, therefore have emerged as a plausible alternative for carbon precursor. In recent years, porous carbons are generally produced from physical (thermal) and/or chemical activation of various types of natural biomass-based carbonaceous materials (e.g. cow dung [13], cotton [14], lignin [15], human hair [16], waste tea-leaves [17], chicken feather [18], chicken eggshell membranes [19], seaweeds [20], nutshell [21], coconut shell [22], coconut fibers [23], corn stalk core [24], pomelo peels [25], ginkgo leaves [26], willow catkins [27], silk cocoon [28], etc. listed in Table 1).

Enteromorpha prolifera (EP) is classified as algae. As a kind of ocean waste, it is such a renewable biological resource of high yield that could grow easily and propagate rapidly under the water body eutrophication and appropriate temperature conditions. Green tide, a phenomenon of massive EP accumulation, is breaking out in the Jiaodong peninsula coast at the end of June to August. It is a serious problem that may do harm to the marine ecosystem, waterways and biodiversity, meanwhile, it would also have a negative effect on aquaculture and tourism industry. Therefore, it is good that these wastes could be recycled or applied for production of value-added products. In this work, we found a practical and feasible solution to solve this problem.

The applications of EP not only provide a cheap raw material for the preparation of activated carbon but also offer an approach for the treatment of this marine biomass [29–30]. Algae, as a nonvascular organism, are a group of eukaryotes protoctista, whose structure is different from wood or coal quality. As we known, there is a lack of sufficient research on the electrochemical properties for algous activated

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Table 1
Recent researches on the porous carbon through high-temperature pyrolysis of natural biomass-based carbonaceous materials.

No.	Name	Temperature °C	Active method	Special surface area $m^2 g^{-1}$	Specific capacitance $F g^{-1}$	Current density $A g^{-1}$	References
1	Cow dung	800	KOH	521	124/117 (non-aqueous electrolyte)	0.1/1	[4]
2	Cotton (T-shirt)	800–1000	NaF		45.4 (1 M Na_2SO_4)	(10 mV s^{-1})	[14]
3	Lignin	850	NaOH/KOH		122 (1 M H_2SO_4)	1	[15]
4	Human hair	800	KOH		340 (6 M KOH)		[16]
5	Waste tea-leaves	800	KOH	2841	330 (2 M KOH)	1	[17]
6	Chicken feather	800	KOH	1839	302 (1 M H_2SO_4)	1	[18]
7	Pistachio nutshell	750	KOH	1069	313 (6 M KOH)	0.5	[21]
8	Coconut shell	900		1874	268 (6 M KOH)		[22]
9	Coconut fibers	850	KOH	2898	266 (6 M KOH)	0.1	[23]
10	Corn stalk core	700	KOH	2495	323 (6 M KOH)	0.1	[24]
11	Pomelo peels	750		1665	214 (6 M KOH)	1	[25]
12	Fallen-leaf	800	KOH	1348.4	302 (6 M KOH)	1	[26]
13	Willow catkins	600	KOH	645	340 (6 M KOH)	0.1	[27]
14	Silk cocoon (N-doped)	700	KOH	3841	408 (6 M KOH)	0.5	[28]
15	*Enteromorpha prolifera*	500		1688			[31]
16	*Enteromorpha prolifera*	750	$H_4P_2O_7$/KOH	926/3500			[32]

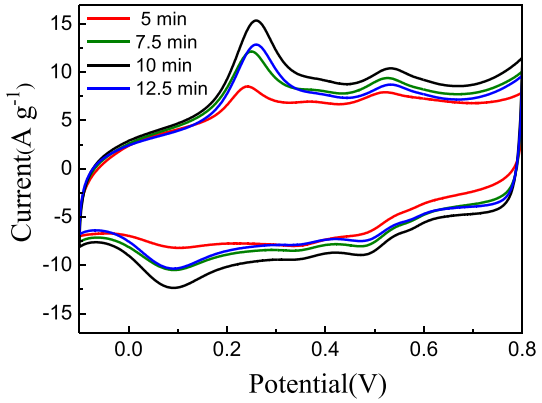

Fig. 1. CV curves with scan rate of 20 mV s^{-1} at different deposition time of PANI.

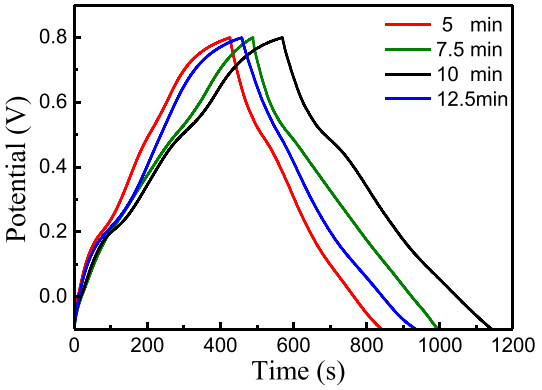

Fig. 2. GCD curves of EPC/PANI at different deposition time of PANI. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

carbon derived from acid and alkali. In addition, to prepare special activated carbon with uniform pore structure distribution (almost complete mesopore or micropore) is an interesting topic. Up to now, there are few reports that can be found in literature, Gao et al. [31] have reported the comparisons of porous, surface chemistry and adsorption properties of carbon derived from EP activated by $H_4P_2O_7$ and KOH. Sun et al. [32] have investigated the adsorption of reactive dyes on activated carbon developed from EP. Gao et al. [33] have studied preliminarily the superior capacitive performance of active carbons derived from EP.

In this work, we proposed EP as carbon source to prepare the porous carbon with the method of high temperature carbonization. The nanostructured PANI/carbon composite electrode was fabricated by the in-situ electrodeposition technique with the obtained porous carbon. The electrochemical behavior of the supercapacitors assembled by the carbon electrode or the PANI/carbon electrode is investigated, respectively. Both supercapacitors have high specific capacitance and good charge-discharge ability, highlighting the promise of these carbons for high power applications.

2. Experimental

2.1. Preparation of active carbon

The EP used in this experiment was collected from Fengcheng beach in Haiyang, China. The EP was thoroughly washed and cleaned to remove any impurities such as attachments and sea salt. Then the EP was put in the fuming cupboard for pre-drying about 1 h. The cleaned and pre-dried EP was put in the freezer dryer at − 40 °C for freeze drying for 24 h. Then the sample was carbonized in tubular furnace under nitrogen flow at 850 °C for 3 h. The resulted carbons were dip in excessive 5 mol L^{-1} HCl solution at 60 °C with heating water bath for 12 h to removing impurities, and then washed with distilled water until the pH value of filtrate was neutral. Finally, the carbons were dried at 60 °C in the vacuum drying chamber for 48 h.

2.2. Preparation of the electrodes

The carbon materials (EPC) were ground with 10 wt% of poly vinylidene fluoride (PVDF) as binder and coated on a platinum sheet (the area of the coating is 1 × 0.5 cm). The carbon and PANI composites were prepared by a controlled in-situ electropolymerization process on a conventional three-electrode system. The prepared carbon electrodes were used as the working electrode and a platinum sheet served as the counter-electrode. All potential values were recorded versus the saturated Ag/AgCl reference electrode. The distance between the working electrode and counter-electrode was about 2 cm. Anodic deposition was controlled by an electrochemical station (CH Instruments 660E, China) in a 1 M HCl electrolyte containing 0.3 M aniline (Sigma-Aldrich, US) monomer. The EPC/PANI composites are prepared with an electrodeposition potential of 0.75 V for a certain period of time. After electrodeposition, the EPC/PANI was washed with deionized water to remove the excessive electrolyte and dried in a vacuum oven at 60 °C. For comparison, the same electrodeposition conditions were used to deposit PANI film on a platinum sheet.