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The reconstruction of char surface by oxidized quantum-size carbon dots under the ultrasonic energy to prepare modified activated carbon materials as electrodes for supercapacitors

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A B S T R A C T

The traditional oxidation of activated carbons (ACs) by chemical oxidants has many defects, such as the destruction of pore nanostructures and the specific surface area, the formation of unstable oxygen functional groups, which can cause negative effects, especially as electrodes for the aqueous supercapacitors, they can also enhance the capacitance fading, and the pseudo-capacitance is not stable. A new strategy was devised to prepare modified AC with the stable surface properties and developed porosity that can solve these problems. Hydrogen peroxide, as a cheap and clean oxidant, was used to modify the biomass-based chars under the ultrasonic energy, so as to improve the chemical and physical properties of ACs. The whole process can be considered as a reconstruction of the carbon surface, the quantum-size carbon dots (CDs) can be released under the ultrasonic energy from the char surface and combined with oxygen free radical species in the liquid phase and eventually return onto the surface. The recombination of free radical species and CDs can not only form stable oxygen groups, but also create more active sites of chars to form the channels, which can generate surface pores of chars before the further formation of pores by activation. The modified ACs have stable oxygen groups, great surface wettability, electrical conductivity, and excellent electrochemical performance. It can be understood that the physical&chemical properties and the electrochemical performance of modified ACs can be significantly improved. The above results can promote the development of modified activated carbon materials and the practical application of aqueous supercapacitors for electric vehicles.

1. Introduction

With the increasing demands and challenges of energy storage, there is an urgent need for developing high-performance energy storage devices and advanced functional materials [1–5]. Activated carbon materials (ACs) as electrodes for supercapacitors have attracted lots of attention because of low cost, high chemical and thermal stability, high specific surface area, excellent electrical conductivity and controlled porosity and abundant pores whose size can be adapted to electrolyte ions [6]. Recently, biomass materials have been widely used as precursors to prepare activated carbon materials, which are very renewable, easily available and low cost [7–9]. However, biomass are mainly composed of cellulose, hemicellulose and lignin, which decompose in the low temperature range of 300–500 °C, obtaining chars with a small content of heteroatoms. ACs are usually prepared under a high temperature, so the surface of ACs have the properties of hydrophobicity and chemical inertness. Hence, the aqueous electrolyte ions cannot wet the surface and enter the pores of ACs adequately. This is one of the reasons why ACs usually have limited specific capacitance (100–200 F g^{-1}) and low energy density (5–10 Wh kg^{-1}) no matter how large their specific surface area and total pore volume are as electrodes for aqueous supercapacitors (SCs) [10].

Therefore, it is necessary to modify the chemical and physical properties of the surface of ACs to improve its electrochemical performance. The metal oxides doped ACs attracted widespread interests recently, but they still have some drawbacks (e.g. poor rate capability and cycling stability), which can limit their practical application [11]. Various heteroatoms doping and surface functional groups can also contribute to the high specific capacitance and high energy density [12–15]. Among these surface groups,

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oxygen groups are the most important because they are abundant and modify the behavior of activated carbons, such as surface wettability, chemical reactivity and electrical conductivity. The chemical oxidation treatments were usually used to add oxygen functional groups onto the surface of activated carbons [16]. According to the previous reports, hydrogen peroxide, as a cheap and clean oxidant, is used to treat activated carbons directly [17]. It can turn into water and oxygen gas after the oxidation process. However, lower H_2O_2 concentration can enhance oxygen groups of activated carbons, which are unstable and worthless. Higher H_2O_2 concentration can destroy the pore structure and reduce the specific surface area of activated carbons inevitably, and in all cases the pseudocapacitance properties are not stable and cause fast capacitance fading. Recently, oxygen-rich precursors have been used to prepare ACs with high amounts of oxygen by one-step carbonization process [23]. However, they have the small specific surface area and poorly developed porosity, which resulted in a high leak current. Therefore, a method that can be used to prepare ACs with both optimal nanostructures and stable oxygen groups incorporated in the carbon framework should be provided for aqueous supercapacitors.

In this paper, a new idea and strategy is provided to modify the biomass-based chars, and therefore to achieve the optimal modification of ACs. The hydrogen peroxide was used to treat the char material with the ultrasonic energy, which resulted in an entirely different phenomenon than the traditional oxidation of ACs treated with hydrogen peroxide directly. The ultrasonic energy in the oxidation of chars has three main effects: First, it cleans the organic impurities and defects in the pores and channels of the chars because it can reduce the Van der Waals' force between particles. Second, it can promote the reconstruction of the chars surface and formation of stable oxygen groups, which can provide a pseudocapacitance in aqueous electrolyte stably. Finally, it can promote the release of quantum-size carbon dots from the char surface and the controllable return during the oxidation reactions, which can then form stable oxygen doping and pores in carbon frameworks. The released carbon dots under ultrasonic energy can combine with oxygen free radical species to form oxidized carbon dots, which can be prove by the following proofs: (1) the reaction mechanism, (2) analysis of test results, (3) the intrinsic properties of carbon dots. So the as-obtained ACs had the high specific surface area, large total pore volume, stable and high content of oxygen groups, great electrical conductivity. The disadvantages of hydrogen peroxide during the traditional oxidation were transformed into optimal conditions to modify chars. Furthermore, the oxygen groups are not only attached to the surface of chars, they are combined with quantum-size carbon dots as oxygen free radical species to reconstruct the surface during the modification. The oxygen atoms can be incorporated into the carbon framework stably and uniformly. Compared with the traditional chemical method, the presence of oxygen can significantly improve the chemical and thermal stability. So the oxygen groups of chars can be kept after high temperature activation.

The oxidation reaction takes place through an electron-transfer reaction similar to the free radical mechanism as shown in Scheme 1 [18]. The reactions can be considered as a reconstruction of the carbon surface. The quantum-size carbon dots (CDs) can be released under the ultrasonic energy from the surface to combine with oxygen free radical species, which are provided by hydrogen peroxide, in the liquid phase or onto the surface of chars. The CDs can be facilely fabricated by chemical oxidation or cutting strategies, so the carbocyclic rings are easily opened to combine with oxygen doping. [19–21] The oxidized CDs also have rich oxygen functional groups at the edge, which provide great aqueous dispersity and subsequent surface functionality. [22] So the chars have rich oxygen surface functional groups and stable chemical bonds with oxygen incorporated in carbon frameworks after oxidation. The recombination of free radical species and carbon dots also create more active sites and pores of chars to form the channels, which can generate surface pores of chars before the further formation of pores by activation. So the oxidation can not only improve the surface properties of ACs, but also benefit the developed porosity. In this paper, a novel strategy is presented to modify biomass-based chars using affordable hydrogen peroxide to clean the surface and release carbon dots under ultrasonic energy in order to reconstruct the char surface and offer stable oxygen species. The UAC samples exhibit promising electrochemical performances as electrodes for aqueous supercapacitors.

2. Experimental section

There were two methods to modify chars to prepare activated carbons. coconut shell was used as raw materials to prepare char in the temperature of 600 °C at a rate of 10 °C min^{-1}. Hydrogen peroxide was used as the oxidation reagent to treat the 5 g chars for oxidation with 100 ml 0%, 1%, 5%, 10%, 20%, 30% hydrogen peroxide under the ultrasonic energy for 1 h when the ultrasonic power was 100 W, respectively. The 100 ml 10% hydrogen peroxide and 5 g char were particularly matching 1:1 M ratio. They were washed and dried at 120 °C for 12 h. The chars were mixed with potassium hydroxide for activation at 1:4 wt in a covered stainless steel vessel and emptied into a muffle furnace at 350 °C for 3 h. Subsequently, the temperature of reactor was raised up to 800 °C for 1 h to prepare AC. The char was also modified by hydrogen peroxide without the ultrasonic energy for comparation. The as-obtained samples were prepared and denoted as shown in Scheme 2.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the variation tendency of surface morphology and porous nanostructures. The porous texture of ACs was also analyzed by N_2 adsorption (77 K) and the samples were degassed at 300 °C in a vacuum for 15 h before all the gas adsorption measurements. The specific surface area (SSA) was

$$C + H_2O_2 \rightarrow C^{+} + OH^{-} + \cdot OH \quad (1)$$

$$C^{+} + H_2O_2 \rightarrow C + H^{+} + \cdot OOH \quad (2)$$

$$\cdot OH + \cdot OOH \rightarrow H_2O + O_2 \quad (3)$$

$$\cdot OHC^{+} + \cdot OOHC \rightarrow H_2O + O_2 + C + C^{+} \quad (4)$$

$$\xrightarrow[\text{the reconstruction of the surface of chars}]{\text{Ultrasonic energy}} H_2O_2 \xrightarrow{C} H_2O + O_2 \quad (5)$$

$$H_2O_2 \downarrow \text{oxidized C}$$

Scheme 1. (1)–(2), the quantum-size carbon dots (CDs) were released from the surface of char, which can combine with the hydrogen peroxide to form oxygen free radical species. (3) the oxygen free radical species can incorporate each other to generate water and oxygen gas. (4) the CDs with oxygen free radical species can reconstruct the surface of chars. (5) the overall reaction, which is similar to the free radical species mechanism.