Enhanced electrochemical performance of graphitized carbide-derived carbon in alkaline electrolyte

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ABSTRACT

A graphitized carbide-derived carbon (CDC), synthesized by chlorination of TiC at 1000 °C, has high specific surface area (SSA), hierarchical micro- and meso-pores, and excellent electrical conductivity. However, the low hydrophilicity leads to poor supercapacitive in alkaline electrolyte. A strategy that introducing oxygen-containing functional groups onto the graphitized CDC by nitrate acid treatment is presented to improve its surface wettability. The treated CDC exhibits a great increase in specific capacitance (from 11.3 to 146 $F\,g^{-1}$) and, most interestingly, an enhanced power capability, a rectangular shape being maintained in CV curves even at the scan rate of 500 $mV\,s^{-1}$. The superiority of the treated CDC is caused by the improved wettability, maintained mesopores and high accessible SSA. Moreover, the introduction of oxygen-containing functional groups contributes the pseudocapacitance of graphitized CDC. Therefore, HNO_3 treatment is a promising way to improve the supercapacitive performance of graphitized carbon materials with mesopores and high specific surface area.

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1. Introduction

Supercapacitors, also called ultracapacitors, have received a great deal of attention in recent years due to their advantageous properties, such as high power density, high capacitance, and excellent performance stability [1,2]. According to energy storage mechanism, the supercapacitor is classified into an electric double layer capacitor (EDLC) and a pseudocapacitor. Charge storage mechanism of the EDLC is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material [3]. Therefore, the large surface area and the porosity of electrode active materials are the basic requirements to achieve high specific capacitance. Carbon materials have been considered as good candidates for supercapacitors because of their high specific area, long cycle life, low cost, and wide use in aqueous and non-aqueous solvents [1,4].

In comparison with traditional porous carbon materials including carbon nanotubes [5,6], graphite [6], or activated carbon [6,7], carbide derived-carbon (CDC), a new type of carbon nanomaterial produced by selective removal of non-carbon atoms from carbide lattice layer by layer [8–10], has recently attracted increasing attention in supercapacitor, since the pores in CDC can be tuned with subangstrom accuracy in a wide range by controlling the chlorination temperature [11,12]. And CDC materials have been considered as good candidates for aqueous supercapacitors [13]. Structurally, the width of pores in CDC increases with increasing chlorination temperature. The CDC chlorinated at lower temperature (<1000 °C), mainly micropores (<1 nm), can exhibit superior specific capacitance due to the desolvation theory [14]. However, the specific capacitance decreases quickly with the increasing voltage scan rate or current density. The CDC synthesized at higher chlorination temperature, which contains mainly mesopores, can provide favorable pathways for ions transport but shows low specific capacitance [15] due to its poor wettability in electrolyte solutions. In our previous work [15,16], a strategy that adding ethanol to alkaline electrolyte is presented to improve the surface wettability of the CDC synthesized at higher chlorination temperature, and the addition of a small amount of ethanol to alkaline electrolyte effectively improves the wettability and corresponding specific capacitance. However, the increasing ethanol content in alkaline electrolyte leads to a monotonous rise in the charge-transfer resistance between electrode and electrolyte, which exerts a negative effect in the power density of the CDC as supercapacitor electrode.

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It has been recognized that surface oxygen-containing functional groups, especially oxygen acidic group (i.e. carboxy, phenol), can be introduced by HNO_3 treatment, and the introduction of the surface functional groups can increase specific capacitance of carbon materials by forming reversible redox pseudo-faradaic capacitor through reacting with KOH electrolytes and increasing wettability of porous surface [17]. Therefore, in this paper, the effect of surface oxygen-containing functional groups introduced by HNO_3 treatment on the supercapacitive performance of the CDC synthesized from TiC at higher chlorination temperature (1000 °C) is investigated. This work attempts to develop an effective technical solution to improve both the specific capacitance and power density of porous carbon materials having poor wettability for supercapacitors.

2. Experimental

2.1. Sample preparation

Commercial available TiC powder (99.5%, ~2 μm, Changsha Xinlan Cemented Carbide Co. Ltd., P.R. China) was used as precursor. The experimental device has been shown in our previous work [18]. CDC powder was obtained as follows: TiC powder (~4 g) was placed in a horizontal quartz tube furnace and heated to the desired temperature (1000 °C) under argon at atmospheric pressure. Once it reached the desired temperature, argon (99.999%) flow was stopped and pure chlorine (99.999%) was passed through the quartz tube at a rate of ~30 ml min^{-1}. Chlorination lasted for 2 hours at the desired temperature. Then, the quartz tube was purged with argon for 30 minutes to blow away the residual chlorine and chlorides gas. And then cool down to room temperature under argon flow. The waste gases were adsorbed by sodium hydroxide solution. The resultant CDC powders were denoted as TiC-CDC.

2.2. Chemical treatment

The treatment of TiC-CDC powders with HNO_3 was carried out as follows: TiC-CDCs were dispersed in HNO_3 (analytical grade) solution with desired concentrations (0 M, 3 M, 6 M and 12 M, respectively) and heated at 70 °C for 2 h, and then cooled down to room temperature. The product was centrifuged and rinsed with deionized water to remove residual HNO_3. Finally, the treated CDCs are dried at 80 °C for 24 h in an ambient atmosphere. The TiC-CDC powders with HNO_3 treatment in a range of 0 to 12 M were denoted as TiC-CDC-0 M, TiC-CDC-3 M, TiC-CDC-6 M and TiC-CDC-12 M, respectively.

2.3. Material characterization

X-ray diffraction (XRD) patterns between 10 and 80 (2θ) degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-Kα radiation (λ = 0.154 nm) operated at 40 kV and 200 mA. Raman spectra from 100 to 3200 cm^{-1} were recorded by using a Renishaw in Via Raman microscope instrument equipped with an Ar$^+$ laser (λ = 514.5 nm) at 50× magnification (~1 μm spot size) and 10% power. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2010 microscope operated at 200 kV. Isotherms adsorption/desorption of N_2 at 77K was carried out using V-Sorb 2800TP specific surface area and pore size
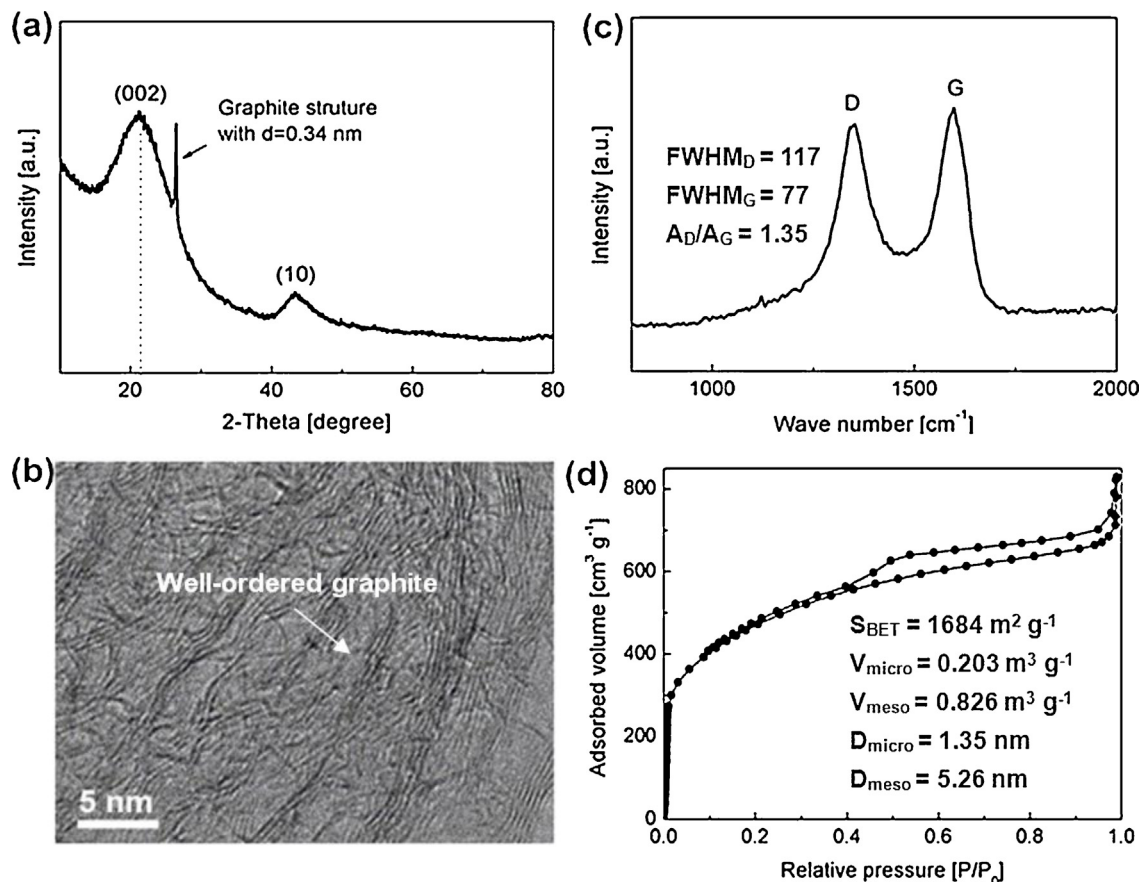

Fig. 1. (a) XRD patterns, (b) Raman spectra, High-resolution TEM images and (d) Low-temperature N_2 sorption/desorption isotherms of TiC-CDC. The insert in (b) is full width at half maximum of D- band (FWHM$_D$) and G- band (FWHM$_G$), and area ratio of D- to G- band (A$_D$/A$_G$). The insert in (d) is BET surface area (S$_{BET}$), HK micropore volume (V$_{micro}$), BJH mesopore volume (V$_{meso}$), HK median pore width (D$_{micro}$), and BJH average pore width (D$_{meso}$).