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Fabrication and enhanced supercapacitive performance of graphene/nano-carbide derived carbon composites

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ABSTRACT

Introducing carbon nanotube (CNT) or carbon black (CB) among graphene sheets has been demonstrated an effective strategy to impede the restacking of graphene sheets and eventually enhances the supercapacitive performance. However, due to their relatively low specific surface area (SSA) and undeveloped pores, the introduced CNT or CB itself has limited contribution to the electrochemical performance. To address the problem, we have synthesized a graphene/nanometer-sized carbide-derived carbon (graphene/nano-CDC) composite. Benefiting from the introduction of the porous nano-CDC, the graphene/nano-CDC composite behaves higher SSA and developed pore structure, and thus superior supercapacitive performance. The specific capacitance of the graphene/nano-CDC composite can reach 195 F g^{-1} at a scan rate of 5 mV s^{-1} , a 179% increase compared with RGO (only 70 F g^{-1}). Most interestingly, even at the scan rate of 5000 mV s^{-1} , its cyclic voltammogram curves can still keep a relatively typical rectangle shape and the capacitance retention can maintain 67% (130 F g^{-1}), approximately 5 times higher than those of the RGO (13%, 9 F g^{-1}). In addition, the specific capacitance of the graphene/nano-CDC composite is quite stable over the entire cycle numbers, and has no significant degradation even after 10,000 cycles.

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Introduction

Supercapacitors or electrochemical double-layer capacitors (EDLCs) are highly promising in many applications where high

power with quick repetitive recharging and long cycle life are needed, such as consumer electronics, medical electronics and electric transportation technology [1–5]. Up to now, lots of the materials as the electrode for supercapacitor, e.g. carbon materials [6], metal oxides [7] and conducting polymers

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[8], have been developed due to their important influence on the supercapacitive performance.

Graphene, a two-dimensional carbon material, is considered as a promising candidate electrode material for supercapacitors due to its high theory surface area, excellent electrical conductivity and stable chemical properties [9,10]. However, the graphene sheets are easy to form irreversible agglomerations due to the strong van der Waals interactions between individual graphene sheets [11–13]. This agglomeration not only decreases the surface area but also limits the access of electrolyte ions into the surface of the graphene sheets. As a result, the actual capacitance value is far lower than the theoretical one. To address this disadvantage, many efforts, including the incorporation of other nanomaterials such as carbon black (CB) [14,15], carbon nanotube (CNT) [16,17] and metal oxides [18,19] among the graphene sheets, have been made. For example, Yan et al. [15] produced graphene nanosheet/CB (GNS/CB) composites, and the specific capacitance of GNS/CB (150.4 F g^{-1}) is higher than that of pure GNS (122.6 F g^{-1}) at 10 mV s^{-1} in 6 mol L^{-1} KOH. Besides, the electrochemical performance of reduced graphene oxide/CB (RGO/CB) hybrid films was investigated by Wang et al. [14], and the specific capacitance of RGO/CB hybrid film is 136.6 F g^{-1} at 0.5 A g^{-1} , which is obviously higher than that (80.0 F g^{-1}) of graphene film without CB at the same current density. It is well accepted that, for the EDLC, its charge storage mechanism is based on the electrostatic adsorption of charge separated ions on the surface of an electrode material [20–22]. Therefore, the large surface area and the porosity of electrode active materials are the basic requirements to achieve high specific capacitance. Unfortunately, due to the very low specific surface area (SSA) of CB (only $\sim 40 \text{ m}^2 \text{ g}^{-1}$ for the graphitized CB [23,24]), the constructed graphene/CB composites behaves relatively low SSA value ($531 \text{ m}^2 \text{ g}^{-1}$ for GNS/CB [15]). Obviously, low SSA value cannot match the requirement to achieve high specific capacitance. As for metal oxides, their incorporation among the graphene sheets can highly improve the specific capacitance, but, unfortunately, will deteriorate the rate performance rapidly [10]. For instance, the specific capacitance of graphene/ MnO_2 composite decreased from 210 to 74 F g^{-1} when the scan rate increased from 2 to 100 mV s^{-1} [18], almost 65% drop in the specific capacitance, which is due to the fact that there is not enough time to accomplish fully the redox process at high scan rate [18,25].

Herein, we propose to introduce nanometer-sized carbide derived carbon (nano-CDC) instead of pure CNT or CB as spacer among the graphene sheets. Due to the high SSA and developed pore structure of the nano-CDC, as well as the effective prevention on the restacking of graphene sheets, the graphene/nano-CDC composite can be expected to exhibit superior supercapacitive performance.

Experimental

Sample preparation

Preparation of nano-CDC and ACDC

Nano-CDC was synthesized by chlorination of β -SiC nanopowder with a particle diameter around 60 nm at 800°C . In

addition, the prepared nano-CDC was further activated by KOH (the weight ratios of KOH/nano-CDC = 7:1), obtaining the activated nano-CDC (denoted as ACDC) sample. The more detailed chlorination and activation are presented in our previous work [22].

Preparation of the graphene/nano-CDC composites

Graphene oxide (GO) was prepared by a modified Hummers' method, which is detailedly described in elsewhere [26].

The stable suspension of GO (1 mg ml^{-1}) and nano-CDC (1 mg ml^{-1}) was produced by ultrasonication. Then, GO and nano-CDC were mixed at a 25% weight ratio of nano-CDC and ultrasonically dispersed for 30 min. Thereafter, 3 ml hydrazine hydrate was added to reduce the GO to the reduced graphene oxide (RGO). The mixture was magnetically stirred at room temperature over night, washed several times by deionized water, and then dried at 90°C for 12 h in vacuum, eventually constructing the G/nCDC composite.

The graphene/ACDC composites (G/ACDC) were also prepared in the same way, and the G/ACDC composites with different ACDC content (25, 45 and 65 wt.%) were denoted as G/ACDC-25, G/ACDC-45 and G/ACDC-65, respectively. In addition, the RGO without nano-CDC was also synthesized by above described method.

Characterization

The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, Hitachi S4800, Japan) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan). X-ray diffraction (XRD) patterns between 10 and $70 (2\theta)$ degrees were collected by Rigaku D/MAX-2500 powder diffractometer with Cu-K α radiation ($\lambda = 0.154 \text{ nm}$) operated at 40 kV and 200 mA. Raman scattering was performed on a Raman spectrometer (Renishaw) by using Ar⁺ laser ($\lambda = 514.5 \text{ nm}$). The N₂ adsorption and desorption analysis was performed at 77 K using the ASAP 2020 instrument (Micromeritics). Prior to analysis, all the samples were degassed in vacuum at 200°C for 8 h. The SSA and micropore volume were calculated by Brunauer–Emmett–Teller (BET) method and t-plot method, respectively. The pore size distribution was determined by non-local density functional theory (NLDFT). The electrical conductivity of samples was measured by the four-point probe technique (ST-2722 powder resistivity tester, Suzhou Jingge Electronic Co. Ltd.).

Preparation of electrode and electrochemical measurement

The electrochemical investigations were carried out in a symmetrical two-electrode cell with a cellulose separator (TF4030, NKK). The working electrodes were prepared as follows: A slurry consisting of 80 wt.% active materials, 10 wt.% carbon black and 10 wt.% PTFE (60 wt.% suspension in water) binder was smeared into nickel foam and dried in vacuum at 120°C for 10 h. Thereafter, the electrode was pressed at a pressure of 10 MPa. The active area of the electrode is 1 cm^2 . The loading mass of active materials is about 1 mg cm^{-2} for each electrode used in this work. 6 mol L^{-1} KOH solution was used as electrolyte. The electrochemical performances of all samples were characterized by cyclic voltammograms (CV) in

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