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Fabrication of graphene and core–shell activated porous carbon-coated carbon nanotube hybrids with excellent electrochemical performance for supercapacitors

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ABSTRACT

Many works have demonstrated that the graphene and carbon nano-tube hybrid (RGO/CNT), synthesized by introducing CNT among graphene sheets, can exhibit improved supercapacitive performance. However, due to its relatively low specific surface area (SSA) and undeveloped pores, the introduced CNT has limited contribution to the electrochemical performance. To solve the problem, we have synthesized a hybrid (RGO/CNT@AC) of graphene and core–shell CNT@AC by introducing activated porous carbon-coated carbon nanotube (CNT@AC) among the graphene sheets. The SSA and micropore volume of RGO/CNT@AC are greatly higher than those of RGO/CNT. Moreover, RGO/CNT@AC shows superior supercapacitive performance compared with RGO/CNT in 6 M KOH electrolyte. The highest specific capacitance is up to 193 F g^{-1} at a scan rate of 10 mV s^{-1}, much higher than that (91 F g^{-1}) of RGO/CNT. Furthermore, RGO/CNT@AC also shows obviously better rate capability (138 F g^{-1} retention at a high scan rate of 5000 mV s^{-1}) and excellent cycling stability (almost 100% capacitance maintaining in cycling stability test). The significant improvement in supercapacitive performance of the RGO/CNT@AC hybrid should be ascribed to the abundant micropores contributed by the AC coated on the CNT surface and more diffusion paths existing between RGO sheets.

Introduction

Supercapacitor, a new energy storage device, has attracted considerable interest in the energy storage field, due to its high power density, rapidly charge/discharge and repeatedly cycle without significant capacitance decay, etc. [1–5]. Up to now, lots of electrode materials for supercapacitors have been investigated, such as graphene [6,7], CNTs/graphene hybrids [8,9], as well as conductive polymers [10–12] and activated carbon [13,14].

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Graphene, a two-dimensional one-atom-thick conductor, is promising as the electrode material for supercapacitors due to its high theory specific surface area (SSA) of 2630 $m^2\ g^{-1}$, excellent electrical conductivity and stable chemical properties and so on [15,16]. However, graphene sheets have an inevitable tendency to aggregation because of the strong van der Waals interactions among individual graphene sheets, which limits the accessibility of electrolyte ions and the surface area utilization [17], and, as a consequence, the capacitance value measured is far lower than the theoretical one. Previous efforts to address this problem include introducing other nanomaterials (such as acetylene black (CB) [18], CNTs [19,20] et al.) among the graphene sheets to impede the restacking of graphene sheets. However, due to the relatively low SSA [21,22], the CB and the CNT introduced among the graphene sheets have little contribution to the electrochemical performance. Unfortunately, this drawback cannot be effectively overcome through the introduction of CB or CNT alone because of the difficulty in constructing abundant pores on CB and CNT [23].

Obviously, introduction of porous carbon among the graphene sheets will be effective to both impede the restacking of graphene sheets and provide high SSA. J. Yan et al. constructed a sandwiched porous carbon layer@graphene hybrid by one-step pyrolysis of the mixture of graphene oxide/polyaniline and KOH, which behaves superior capacitive performance [24]. Herein, we propose another strategy that constructs porous carbon/graphene hybrids, i.e., synthesis of a RGO/CNT@AC hybrid by introducing the activated porous carbon-coated carbon nanotube (denoted as CNT@AC) instead of pure CNT among the graphene sheets. This architecture inherits the advantages of graphene and CNT (high electrical conductivity) as well as porous carbon (huge surface area) [25]. Due to the high SSA and developed pore structure of the activated porous carbon coating (AC), more electrolyte ions diffusion pathways between graphene sheets, as well as the effective prevention on the restacking of graphene sheets by CNT@AC, the RGO/CNT@AC hybrid can be expected to exhibit superior supercapacitive performance.

Experimental

Sample preparation

Preparation of graphene oxide (GO) powders

Graphene oxide (GO) powders were obtained by a modified Hummers' method as described in literature [19,26]. In brief, 2 g graphite and 1 g $NaNO_3$ were added into a 250 ml flask filled with 46 ml H_2SO_4 (98%) in ice bath under stirring. Next, 6 g $KMnO_4$ was slowly added to the solution over about 1 h, and, in the mean time, the ice bath was used to keep the temperature of the solution below 10 °C. After adding $KMnO_4$, the ice bath was removed and the solution was heated to 50 °C, followed by a slowly addition of 80 ml deionized water. And then temperature of the solution was raised to 90 °C and maintained for 30 min. Next 60 ml deionized water with 10 vol. % H_2O_2 was added to the solution until the reaction was terminated. The resultant solution was centrifuged and washed by 10 wt. % HCl and deionized water to completely remove the impurities, and, finally, dried at 60 °C for 12 h to obtain the GO powders.

Preparation of activated porous carbon coated carbon nanotube (CNT@AC)

0.05 g nitric acid-treated CNT (20–40 nm in diameter, obtained from the Shenzhen Nanotech Co. Ltd. of China) with 2.5 g glucose was added into 100 ml deionized water and ultrasonically dispersed for 3 h. Then, the resultant mixture was put into Teflon-sealed autoclave with a fill rate of 80%. After 15 h hydrothermal treatment at 190 °C, the produced black powders were further carbonized in a tube furnace at 800 °C for 2 h in argon atmosphere, thus obtaining a core–shell pristine carbon-coated CNT composite (denoted as CNT@PC).

The as-prepared CNT@PC was activated by KOH at 800 °C for 1 h in argon atmosphere. Thereafter, the activated sample was immersed in 10 wt. % HCl solution, then washed to neutral and dried at 100 °C for 10 h, thereby achieving core–shell activated porous carbon-coated CNT composite (CNT@AC).

Preparation of graphene/CNT@AC hybrids (RGO/CNT@AC)

GO powder was added into 50 ml deionized water and dispersed by ultrasonication for 1 h. Then, the obtained CNT@AC was mixed with GO with a weight ratio of 2:8 and ultrasonically dispersed for 2 h. Thereafter, 5 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 by deionized water until to neutral, and then dried at 60 °C for 12 h, eventually constructing the graphene/CNT@AC hybrid (RGO/CNT@AC).

To probe into the effect of KOH amount, the as-prepared CNT@PC were activated by using different weight ratios of KOH to CNT@PC (0:1, 2:1, 4:1, 6:1 and 8:1), and the corresponding RGO/CNT@AC hybrids are denoted as RGO/CNT@PC, RGO/CNT@AC-2, RGO/CNT@AC-4, RGO/CNT@AC-6 and RGO/CNT@AC-8, respectively.

RGO/CNT hybrid was also prepared by mixing the pristine CNT (without AC coating) and the RGO in the same way. For comparison, the CNTs with equal quantity were added in the RGO/CNT and the RGO/CNT@AC hybrids. In addition, the amount of the estimated RGO as well as CNT and porous carbon in the RGO/CNT@AC hybrids was list in the Supplementary material.

Characterization

The morphologies and microstructure of the samples were observed using a Hitachi S-4800 field emission scanning-electron microscopy (SEM) at 15 kV and a JEM-2010 transmission electron microscopy (TEM) at 200 kV. X-ray diffraction (XRD) patterns between 10 (2θ) and 60 (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. Gas adsorption/desorption analysis was done in the V-Sorb 2800TP surface area and pore distribution analyzer (Gold APP Instruments Corporation, China) with N_2 as adsorbent at 77 K. Prior to analysis, samples were degassed in vacuum at 200 °C for 8 h. The SSA, according to BET (Brunaure, Emmet and Teller) theory and nanopore volume, was calculated by using

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