Short communication

Self-assembly of disordered hard carbon/graphene hybrid for sodium-ion batteries

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HIGHLIGHTS

- Disordered hard carbon/graphene hybrid was successfully prepared.
- Unique structure with carbon layers and numerous microspheres growing on graphene.
- High capacity and rate capability as anode material for SIBs.

ARTICLE INFO

ABSTRACT

Disordered hard carbon/graphene (C@G) hybrid is successfully designed and prepared for the first time through a facile route. SEM and TEM analyses show the uniform distribution of carbon microspheres and carbon layers on the surface of graphene. As an anode material of sodium-ion batteries, such a construction could ensure an effective contact area with the electrolyte and offer massive active sites. It displays a stable sodium storage capacity of ~300 mAh g^{-1} after 100 cycles at a current density of 50 mA g^{-1} and exhibits an excellent rate performance. The unique structure and advantageous synergistic effect between disordered hard carbon and graphene make a significant contribution to the good Na$^+$ insertion/extraction property.

1. Introduction

Lithium-ion batteries (LIBs) are important energy storage devices with high energy density, long cycle life and environmental benignity [1–3]. Although LIBs have been prosperous in portable electronics, they face many challenges such as high cost and limited lithium source. Advanced energy storage devices are urgently needed to satisfy the continuously increasing demand. Sodium-ion batteries (SIBs) are one of the promising candidates as power source and possible substitute of LIBs [4,5]. Recently, SIBs have drawn much attention due to their similar electrochemical mechanism, comparatively low cost and abundant sodium source [6].

However, suitable anode materials with higher sodium storage capacity, longer cyclic and faster charge–discharge rate performance still remain challenging [7]. The typical graphite as dominant commercial anode material of LIBs shows poor electrochemical performance in SIBs because of the larger ionic diameter of sodium [8]. Lots of attempts have been made to explore suitable anode materials to meet the demand of energy storage equipment [9,10]. Among those candidates, hard carbon materials with low degree of graphitization and larger interlayer space hold good prospect. To date, diverse carbon nanostructures from different precursors (including biomass and polymers) have been designed successfully, e.g. nanofibers [11], nanosheets [12], hollow nanospheres [13]. These works have demonstrated that hard carbon materials with attractive morphology could improve the electrochemical performance. Graphene with excellent electronic conductivity and thermal stability has been paid widely attention. As an anode material of SIBs, it ensures good electronic transmission channel and structural stability [14]. Moreover, the structure with two-dimensional thin layers can not only shorten Na$^+$ diffusion path, but also possess higher sodium storage potential. Therefore,

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disordered hard carbon/graphene hybrid with unique morphology could be a reasonable design to further enhance the electrochemical performance of anode material for SIBs.

In this article, we construct a novel disordered hard carbon/graphene (C@G) hybrid by in situ synthesizing graphene-like carbides with abundant carbon microspheres on the surface. The unique structure can accelerate mass transport effectively by providing a large contact area with the electrolyte and a short Na$^+$ diffusion path. As a consequence, the obtained C@G exhibits a stable reversible capacity and an excellent rate performance.

2. Experimental

All chemicals were of analytical grade and used directly without further purification. In a typical process, graphite oxide was synthesized by a modified Hummers' method [15]. Briefly, 5 g sucrose and 225 mg graphite oxide were dissolved in 75 mL deionized water followed by sonication for 3 h. The obtained suspension was transferred to a 100 mL Teflon-sealed autoclave and maintained at 190 °C for 12 h. After cooling down to room temperature, the resultant product was washed with deionized water and dried in a vacuum at 60 °C. Finally, C@G hybrid was obtained after calcining at 700 °C for 2 h in N$_2$ atmosphere. For comparison, pure carbon powder (CP) without adding graphite oxide and pure graphene (GN) without adding sucrose were synthesized by the same method as mentioned above.

The morphologies of obtained samples were investigated using field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan), transmission electron microscopy (TEM, JEM-2100UHR, Japan). X-ray diffraction (XRD) analysis was recorded on X'Pert PRO MPD (Holland) with Cu Kα radiation. Raman analysis was performed on a Jobin Yvon HR800 Raman spectrometer. Nitrogen adsorption−desorption isotherms were carried out on ASAP 2020 Micromeritics instrument. X-ray photoelectron spectroscopy (XPS) was performed on Thepermo ESCALAB 250XI with a monochromatic Al K X-ray source.

The sodium coin cells were assembled in an argon-filled glove box by using pure sodium foil as the counter and reference electrode. The electrolyte was 1 M NaClO$_4$ in ethylene (EC) and diethyl carbonate (DEC) (v:v = 1:1). The working electrodes were prepared by pasting the slurry of the active materials (80 wt.%), carbon black (10 wt.%) and poly(vinylidene) fluoride (10 wt.%) in N-methyl-2-pyrrolidinone on Cu foils. Then dried at 100 °C in a vacuum for 10 h. Galvanostatic charge−discharge measurements were performed on a Land CT2001A cycler. Cyclic voltammetry (CV) tests were carried out on a CHI660D Electrochemistry Workstation at a scan rate of 0.1 mV s^{-1} between 0.01 and 3 V. Electrochemical impedance spectroscopy (EIS) studies (signal amplitude, 10 mV; frequency range, 0.01−100000 Hz) were measured on Ametek PARSTAT4000 electrochemistry workstation.

3. Results and discussion

The detailed surface morphologies and microstructure of as-obtained samples were studied by SEM and TEM. Fig. S1A displays SEM image of GN. Flexible graphene sheets and some obvious corner angles on the surface can be found. From SEM image of CP (Fig. S1B), numerous carbon microspheres inherit an interconnected structure, which is consistent with the reported literature [16]. As shown in Fig. 1A, abundant carbon microspheres grow uniformly on elastic graphene skeleton, as seeds germinate in the field and then sprout out to grow into carbon microspheres. No separated carbon microspheres are observed, suggesting carbon microspheres around 450 nm are attached on graphene framework. TEM image of GN (Fig. S2) shows typical thin film-like structure

with transparent surface and numerous wrinkles which reflect the corner angles have been observed in Fig. S1A. Fig. 1B depicts TEM image of C@G, the surface of graphene sheets are coated with carbon layers and the wrinkles exhibit nanotubular structure around 45.8 nm of diameter. The green arrows are corner angles of graphene, while the yellow arrows correspond to carbon layers. The TEM image also reveals the clear outline of carbon microspheres. Through SEM and TEM observations, it can be concluded that carbon microspheres were grown on the surface of carbon layers which distributed uniformly on the graphene sheets.

The XRD pattern of the as-prepared C@G is illustrated in Fig. 2A. As can be seen, it presents two broad, weak diffraction peaks corresponding to the (002) and (100) diffraction modes at about 23.7° and 43.4°, characteristic of a disordered carbonaceous structure. The interlayer spacing (d$_{002}$) is calculated to be ~0.375 nm, which is obviously larger than that of graphite (0.335 nm). It is worth noting that the large interlayer distance would facilitate the reversible Na$^+$ storage and transport [13]. Raman spectroscopy was employed to investigate the graphitization degree of C@G. As displayed in Fig. 2B, it confirms the presence of D band (1341 cm^{-1}) and G band (~1587 cm^{-1}) of amorphous carbon. D band results from disorder, structural defects and associates with the formation of sp^3 defect bonds [17]. G band corresponds to the structural integrity of graphite. The intensity ratio (I$_D$/I$_G$) of C@G is 0.934, higher than 0.773 of CP, indicating abundant defects and evident disordered carbonaceous structure in C@G. The presence of defects could favor Na$^+$ diffusion [18] and provide more adsorption sites by increasing charge transfer between adatoms and defects [19].

The specific surface area and pore structure of GN and C@G hybrid were further characterized by nitrogen adsorption−desorption isotherms. GN exhibits major pore size distributions in the meso- and macroranges with a BET surface area of 399 m^2 g^{-1} and an average pore size of 14.4 nm (Fig. S3). C@G hybrid displays a larger BET surface area of 488 m^2 g^{-1} and mainly possesses micropores with an average pore diameter of 1.6 nm (Fig. 2C). The highly dispersed carbon microspheres and carbon layers on the surface of graphene contribute to the increase in the surface area and decrease in the mean pore size compared with that of pure GN. The pore structure agrees well with that of sucrose-derived hard carbon reported previously [20]. The high surface area could offer a large electrode/electrolyte contact area and provide Na$^+$ with more active sites [13,21], while porosity largely influences the Na$^+$ adsorption ability, especially micropores according to the mechanism for sodium insertion [22].

The full-range XPS spectrum of C@G in Fig. S4 shows a significant XPS C1s peak at about 285 eV (97.02 at%), along with a much weaker O1s peak at about 534 eV (2.98 at%), indicating only a few oxygen-containing functional groups exist. The C1s XPS spectra (Fig. 2D) analysis indicates that the strongest peak of sp^2 carbon appears at a binding energy of 284.6 eV. In addition, there are other weaker peaks such as sp^3-bonded carbon (285.4 eV), C−O (286.6 eV) and C=O (288.5 eV) [23]. The low content of C=O indicates that most carboxyl and hydroxyl functional groups were reduced [24]. The existence of a few oxygen-containing groups could enhance the sodium uptake [25,26] and contribute to Na storage [27] though it may lead to initial irreversible Coulombic efficiency [24].

The electrochemical behavior of C@G as anode material of SIBs was investigated by CV and galvanostatic charge−discharge measurements. Fig. 3A displays CV curves of C@G electrode for the first three cycles from 0.01 to 3 V at a scanning rate of 0.1 mV s^{-1}. In the first CV scan, noticeable cathodic peaks are observed at 1.02 V, 0.42 V and near 0.02 V. The small peak at 1.02 V is ascribed to the reaction of sodium with functional groups at the electrode surface [13]. The large irreversible reduction peak at 0.42 V is attributed to