CrossMark

Ball-milling preparation of one-dimensional Co–carbon nanotube and Co–carbon nanofiber core/shell nanocomposites with high electrochemical hydrogen storage ability

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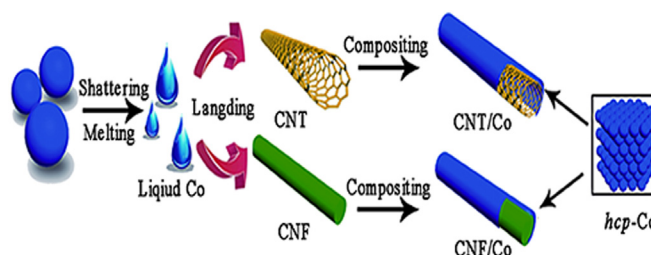[b] College of Science, Harbin Engineering University, Harbin, Heilongjiang 150001, PR China
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HIGHLIGHTS

- 1D CNT (CNF)/Co nanocomposites were synthesized by a ball-milling method.
- Co shell with diameter of 4 nm has been successfully coated on CNT.
- The composites exhibited good hydrogen storage performance.

GRAPHICAL ABSTRACT

ABSTRACT

Owing to the special honeycomb structures and excellent electrical characters of carbon nanotube (CNT) and carbon nanofiber (CNF), they are extensively considered as ideal cornerstones for hydrogen storage materials. Herein, metal cobalt has been uniformly coated on CNT's and CNF's surfaces in nanoscale through a simple ball milling process. Accordingly their X-ray diffraction, scanning electron microscope and transmission electron microscopy measurements clarify the satisfying composite structures. And their electrochemical experimental results demonstrate that the as-obtained CNT/Co and CNF/Co composites have excellent electrochemical hydrogen storage reversibility and considerably high storage capacities of 717.3 mAh g^{-1} (2.62 wt% hydrogen) and 739.4 mAh g^{-1} (2.70 wt% hydrogen) under room temperature and ambient pressure, which are much higher than the capacities of individual CNT (29.9 mAh g^{-1}, 0.11 wt% hydrogen) and CNF (49.0 mAh g^{-1}, 0.18 wt% hydrogen) measured in this work. Furthermore their hydrogen storage processes and the mechanism have also been investigated, in which the quasi-reversible CNT (CNF)/Co $\leftrightarrow$ CNT (CNF)/Co–H$_x$ reaction is the dominant cycle process.

1. Introduction

Recently the research on energy materials is of utmost importance regarding for energy harvest and energy storage. Hydrogen, as a renewable resource free of pollution, is very promising for application in future. However, the major impediment is that it is difficult to be high-capacity stored within an effective, safe and

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stable solid-state medium, which restricts its practical application [1–4]. So highly efficient and convenient hydrogen storage materials and technologies become challenges for today's development of hydrogen economy [5–7]. Therefore, many storage mediums have been developed to uptake as much as possible hydrogen, such as metal alloys, metal-organic frameworks and carbon nanotubes etc [8–14]. Because carbon nanotube (CNT) and carbon nanofiber (CNF) have special one-dimensional (1D) nanostructures (resulting in their good dispersibility and operability) and multiaperture geometrical structures (providing a large specific surface) [15], they have been considered as ideal cornerstone materials for improving the capacities of hydrogen storage materials [16–19]. Some works have been conducted to modify the above carbon frameworks, such as titanium, cobalt and magnesium etc [20–22]. Among these materials, metal Co is a desired candidate for absorbing hydrogen [23]. Recently, a series of cobalt−carbon materials [12–14,20,24–26] are reported to have high reversible absorption/desorption hydrogen capacities and good cycle life as negative electrode materials of electrochemical hydrogen storage cells, and their electrochemical hydrogen storage capacities are obviously improved after mixing some nonmetallic materials, as shown in Table 1.

It has been reported that CNT/Co was obtained through a ball-milling treatment at a lower speed of 450 r min^{-1} for 10 h, which reached the capacity of 402.5 mAh g^{-1} (1.48 wt% hydrogen) for electrochemical hydrogen storage [12]. Compared with the theoretical hydrogen storage capacities of individual metal Co (3.32 wt% hydrogen) [31], the capacity obtained is not satisfied, which may be due to efficient grain refinement and the weak composite structures under a lower activation energy provided by a lower speed ball-milling (BM). Considering the reaction between metal Co and carbon materials for Co$_3$C compound when the ball-milling speed nearing 800 r min^{-1} [12], a suitable ball-milling speed (600 r min^{-1}) is selected in this work to attempt to obtain Co and CNT (CNF) composites with higher hydrogen storage capacity. And it is found that the as-prepared composites (CNT/Co and CNF/Co) exhibit excellent electrochemical hydrogen storage capacity of 717.3 mAh g^{-1} (2.62 wt% hydrogen) and 739.4 mAh g^{-1} (2.70 wt% hydrogen). Also their hydrogen storage processes and the mechanism have been proved as a quasi-reversible CNT (CNF)/Co ↔ CNT (CNF)/Co−H$_x$ reactions happening at three different locations for the dominant cycle process, which was not observed before.

2. Experimental

Metal Co powders (purity 99.9%, 200 mesh, Shanghai Xingzhi chemical factory) were firstly mixed with CNT or CNF (Shenzhen Namigang Co. Ltd.) with the mass ratio of 5:1. In a typical experiment, all samples were ball-milled using a planetary ball mill (pulverisette 7, FRITSCH) in a ZrO$_2$ vessel at the speed of

Table 1
Preparation methods and hydrogenation capacities of pure Co and cobalt−carbon composites.

Materials	Preparation method	Storage capacity (wt% hydrogen)
Co [24]	Chemical precipitation	1.29
Co−CNT [20]	Ball milling (450 r min^{-1}, 10 h)	1.48
Co$_3$C [12]	Ball milling	5.176
Graphene−porous cobalt [13]	Chemical precipitation	0.89
Cobalt graphene [14]	Ball milling	3.29
Cobalt−mesoporous carbon [25]	Chemical precipitation	0.45
Cobalt−carbon aerogels [26]	Chemical precipitation	4.38

600 r min^{-1} for 2–10 h under Ar atmosphere. The mass ratio of ball to powder was maintained at 10:1. After cooling to room temperature, the obtained powders were collected and characterized by X-ray diffraction (Rigaku D/max IIIA, Cu Kα). The scan rate of 0.05° s^{-1} was used to record the patterns in the 2θ range of 10–70°. Scanning electron microscope (SEM) image was obtained by a JSM-6700F field emission scanning electron microanalyser (JEOL, Japan), whereby the powders were mounted on a copper slice. Transmission electron microscopy (TEM) and High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The electrochemical measurements were carried out following the method reported with slight modification [43]. Briefly, the electrodes were prepared by mixing CNT/Co or CNF/Co powders, acetylene black and polytetrafluoroethylene at the weight ratio of 7:2:1, which was pressed onto a porous nickel mesh at 50 MPa. Experiments were performed in a two-electrode cell in 6 mol L^{-1} KOH at 25 °C under normal atmosphere, Ni(OH)$_2$ as the counter electrode. The cycle life and charge−discharge curves were tested by a LAND battery-test instrument (CT2001A). The negative electrodes were charged at a current density of 100 mA g^{-1} for 8 h, and then discharged to 0 V at a current density of 30 mA g^{-1}. Furthermore, in order to study the rate capability of the composites, the negative electrodes were discharged to 0 V at current density of 200–1000 mA g^{-1}. The cyclic voltammetry (CV) was conducted by using an electrochemical workstation (CHI660D) of three-electrode test cell. The cell consisted of the composites as the working electrode, metal platinum gauze as the counter electrode, an Ag/AgCl electrode as the reference electrode, and the electrolyte was 6 mol L^{-1} KOH.

3. Results and discussion

3.1. Structure and morphology of CNT/Co composite

Firstly, the overall crystalline and purity of the raw materials are investigated by XRD diffraction. As shown in Fig. 1(a), the raw Co powder has two phases: *fcc* phase (PCPDF 15-0806) and *hcp* phase (PCPDF 89-4308). And the XRD pattern of raw CNT displays two strong diffraction peaks at 26.5° and 42.4°, which can be attributed to the hexagonal graphite structures (PCPDF 26-1076). After ball-milling the precursors for several hours at 600 r min^{-1} under Ar atmosphere, it is found that all diffraction peaks corresponding to Co are broadened, as shown in Fig. 1(b) which indicates that the Co crystalline grains are refined. In addition, the transformation of *fcc*-cobalt into *hcp*-phased has also been observed. As reported, that lattice surface energy of *fcc*-Co (~2.05 × 10^{-18} J per unit lattice) is lower than that of *hcp*-Co (~2.61 × 10^{-18} J per unit lattice), and *hcp*-Co is a more stable phase [27]. Also the sample's average crystallization size of metal Co is 3.4–4.4 nm calculated by the Scherrer equation from the XRD results, which implies the efficient refinement process in this work.

To investigate the composites' morphologies and composite status and screen out the optimum composite machining condition for their ball-milling preparations, SEM examinations of the ball-milled composites are carried out. Fig. 2(a)–(c) shows the SEM images of pure CNT and CNT/Co composites ball-milled for 4 h and 6 h. It can be seen that uniform 1D composites form and rare individual metal Co particle is observed. It is also found that the diameters of the final products change to ~48 nm after ball-milling the CNT (~40 nm) and metal Co for 4 h and 6 h, respectively, which implies that metal cobalt has been well coated on the surfaces of CNTs. As the ball-milling times are extended from 4 h to 6 h, the CNTs are cut off and their lengths of the 1D product are significantly reduced, as shown in Fig. 2(b) and (c). So the 4 h is the suitable ball-