Materials Letters 108 (2013) 196–199

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Investigation of graphite/carbon spiral nanoribbons using $FeCl_3$–$CuCl_2$–graphite intercalation compounds as precursors

Liuyue Cao, Li Yang*, Hongbo Liu, Yuxi Chen, Xiaohong Xia, Haibo zhao

School of Material Science and Engineering, Hunan University, Changsha, Hunan 410082, China

ARTICLE INFO

Article history:
Received 23 May 2013
Accepted 27 June 2013
Available online 8 July 2013

Keywords:
Carbon nanoribbons
Spiral morphology
Graphite intercalation compounds
Hybrid structure
Chemical vapor deposition
Catalyst

ABSTRACT

$FeCl_3$–$CuCl_2$–graphite intercalation compounds (GICs) were applied to synthesize graphite/carbon spiral nanoribbons (G/CSNRs) by chemical vapor deposition (CVD) of acetylene and hydrogen. The G/CSNRs were characterized by XRD, SEM and Raman spectra. The XRD patterns confirmed the G/CSNRs did contain graphite. The as-grown CSNRs were thin and twisted, owning a width of ~92 nm, a thread pitch of ~56 nm and a length in micrometer scale. The Raman spectra showed the imperfect crystallinity of CSNRs. During this CVD process, $FeCl_3$–$CuCl_2$–GICs acted as providers of graphite substrates as well as catalyst carriers. The CVD method mediated by GICs also provided possibilities to design and prepare a variety of hybrid carbon structures.

1. Introduction

The study of carbonaceous material with spiral morphologies is of great interest in recent years due to their extraordinary mechanical, electrical and field emission properties [1–4]. Among the variety of methods to synthesize such special carbon materials, chemical vapor deposition (CVD) is the most popular one. And the typical requirements include: (i) an appropriate carbon source, (ii) growth catalysts such as Fe, Co, Ni, (iii) promoter elements such as P, S and (iv) inducer metals such as Cu, Sn, In [5–8].

Graphite intercalation compounds (GICs) are formed by the insertion of atomic or molecular layers of a different chemical species (usually called intercalant) between graphene layers. Many of these compounds require encapsulation to ensure chemical stability, with intercalants being easily oxidized or deintercalated. However, graphite compounds intercalated by certain metal chlorides such as $FeCl_3$, $CuCl_2$, $NiCl_2$, etc. are relatively stable in air at temperature below 80 °C. If the temperature increases, the metal chlorides of the GICs will then deintercalate through the edges or other defective sites of the graphite crystal. In addition, most metal chlorides can be intercalated into graphite only under a certain pressure of chlorides. But $FeCl_3$ can give off chlorine by its own disproportionation, which means it can be intercalated into graphite without any intentional addition of chlorine gas pressure [9]. Therefore, to make procedure and equipment safe and simple, we used $FeCl_3$ as one of intercalants for the synthesis of ternary $FeCl_3$–$CuCl_2$–GICs. Then taking advantage of its unique release mode of molecular intercalants, $FeCl_3$–$CuCl_2$–GICs were applied as catalyst carriers and graphite substrates, and acetylene as carbon source to fabricate a hybrid structure of graphite/carbon spiral nanoribbons (G/CSNRs). The potential synergetic effect of graphite and carbon spiral nanoribbons makes the hybrid carbon materials promising in various conductive, mechanical, magnetical and other applications. Moreover, CVD mediated by GICs was identified to be an efficient way to prepare hybrid carbon structures.

2. Experimental

The preparation of $FeCl_3$–$CuCl_2$–GICs: Natural flake graphite, anhydrous ferric chloride and anhydrous cupric chloride were mixed at a mole ratio of 30:8:2 in an aluminum oxide pot, and then along with the pot, the reactants were encapsulated into a stainless steel container and sealed off. The mixture was heated at 550 °C for 12 h. Subsequently, the products were washed with diluted HCl and distilled water and dried at 80 °C for 24 h.

The synthesis of G/CSNRs: $FeCl_3$–$CuCl_2$–GICs were stuck on the copper adhesive fixed on a ceramic substrate in a quartz tub. After the tube was closed and purified by argon, acetylene and hydrogen were flowed in at the rates of 3.3 sccm and 6.7 sccm respectively. After the temperature had been kept at 720 °C for 30 min, acetylene and hydrogen flow were immediately stopped and the tube was flushed with argon to remove the residual acetylene and hydrogen. Finally, the reaction tube was cooled to room temperature.

Morphology and structural characterizations: X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8-Advance

* Corresponding author. Tel.: +86 13574836840.
E-mail address: hunanyangli@aliyun.com (L. Yang).

0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.06.114

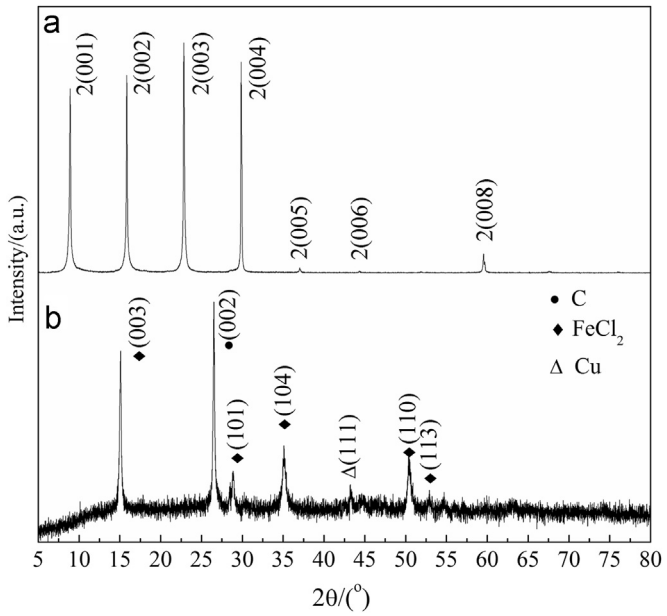

Fig. 1. XRD patterns of (a) $FeCl_3$–$CuCl_2$–GICs and (b) as-synthesized CVD products.

diffractometer with Cu Kα radiation. The morphology of the as-obtained materials were characterized by scanning electron microscope (SEM) JEOL JSM-6700F. Raman spectra were examined with LABRAN-010 Laser Confocal Raman Spectrometer.

3. Results and discussion

XRD characterizations were conducted to depict crystal structures of $FeCl_3$–$CuCl_2$–GICs and as-synthesized CVD products. Fig. 1a shows that the graphite was intercalated to stage 2 with metal chlorides, which indicated catalyst precursors were successfully carried. After CVD process (Fig. 1b), the stage structure of GICs disappeared. Instead, graphite, $FeCl_2$ and a small portion of Cu were obtained. It meant that accompanied by the metal chlorides' deintercalation and evolution into $FeCl_2$ and Cu, graphene layers restored to graphite structure.

The SEM images of $FeCl_3$–$CuCl_2$–GICs and its CVD products are listed in Fig. 2. The $FeCl_3$–$CuCl_2$–GICs displayed multi-layered plates like natural flake graphite (Fig. 2a). After the deposition procedure, the products appeared in a hedgehog-like morphology (Fig. 2b). The "prickles" of the samples were too flourished to identify the graphite substrate but only an ambiguous profile of

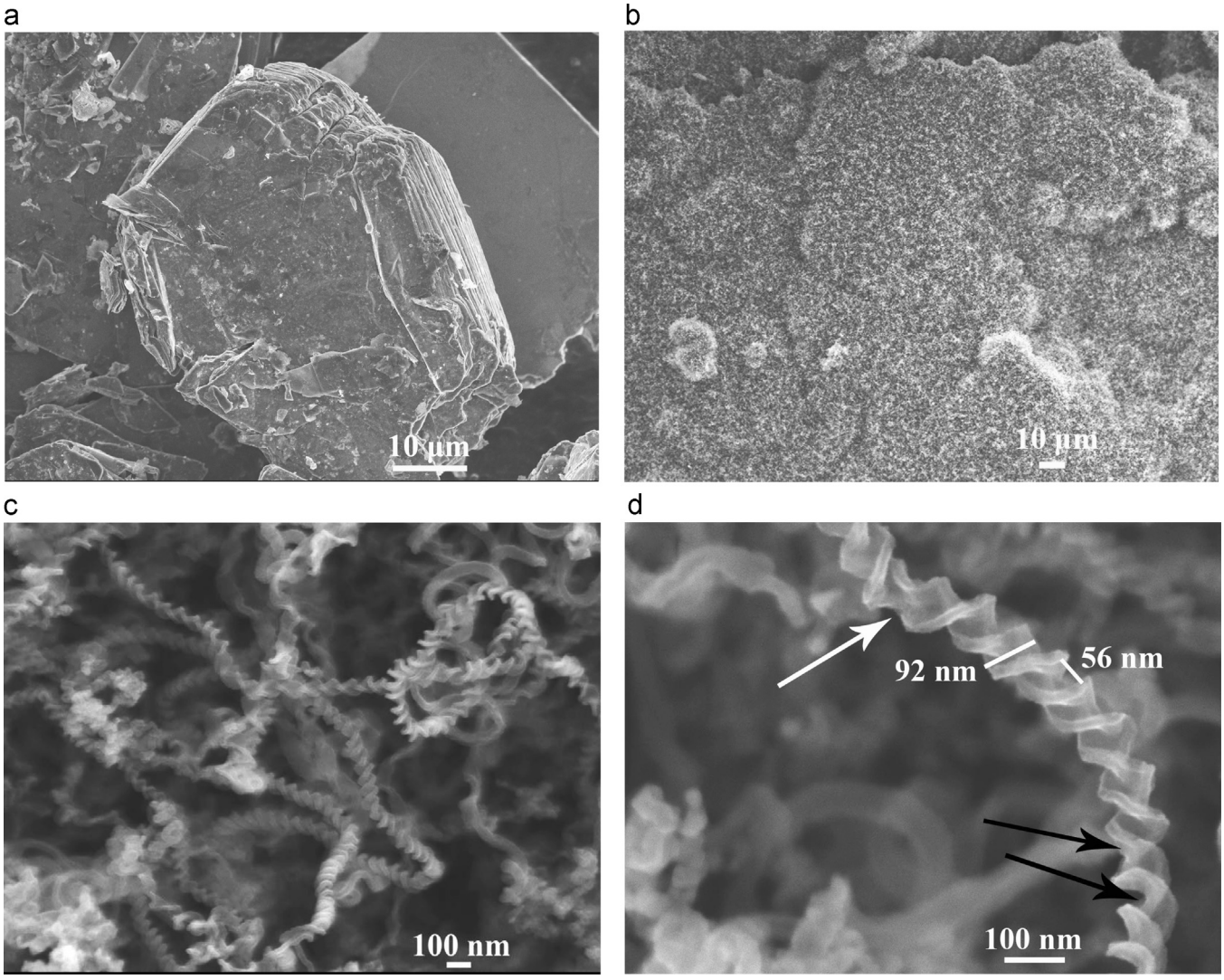

Fig. 2. SEM images of (a) $FeCl_3$–$CuCl_2$–GICs and (b–d) its CVD products.