Materials Chemistry and Physics 127 (2011) 397–404

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Characterization of carbon nanomaterials synthesized from thermal decomposition of paper phenolic board

Yu-Ting Huang, Yi-Wei Lin, Chih-Ming Chen*

Department of Chemical Engineering, National Chung-Hsing University, 250 Kuo-Kuang Rd., Taichung 402, Taiwan

ARTICLE INFO

Article history:
Received 23 September 2010
Received in revised form 12 January 2011
Accepted 12 February 2011

Keywords:
Nanostructures
Chemical synthesis
Vapour deposition
Chemical techniques

ABSTRACT

The carbon nanomaterials are synthesized at 800–1000 °C using paper phenolic (PP) board and $NiCl_2$ aqueous solution as the carbon source and catalyst precursor, respectively. The products include hollow-cored, multi-walled carbon nanofibers (CNFs), platelet-stacked-type CNFs, nanocapsules, and cup-stacked-type CNFs. It is suggested that the catalyst shape plays an important role in the microstructure of the carbon nanomaterials. Since the PP board is used as the insulating substrate of printed circuit board (PCB), the results of this study show that recycling the waste PCBs and using their PP boards to synthesize valuable carbon nanomaterials are of high feasibility.

1. Introduction

Nanomaterials have attracted considerable interest during the past few decades because of their distinctive properties and high potential in a wide range of technological applications. Carbon nanomaterials, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), and carbon nanosheets (CNSs), are the representatives of promising nanomaterials. They have excellent physical and chemical properties, such as superior thermal and electrical conductivities, high strength, light weight, high surface area, and good chemical stability. These characteristics make their applications successful in the anode materials of lithium-ion batteries [1,2], biomaterials [3,4], fuel cells [5,6], biosensors [7], field emission devices [8], and hydrogen storage materials [9].

The key material in the synthesis of carbon nanomaterials is the carbon source that can provide the carbon species. In general, carbon-containing substances can potentially act as the carbon source as long as an appropriate synthesis technique is employed. The hydrocarbon gases have been widely used as the carbon sources because they have simple chemical structures which easily decompose to release the carbon species by means of catalyst-assisted [10] or plasma-enhanced [11,12] chemical vapour deposition (CVD) methods. Using the ultra-high temperature arc-discharge method, even chemically stable graphite can also decompose and release the carbon atoms for the formation of carbon nanomaterials [13].

A printed circuit board (PCB) is used to mechanically support and electrically connect electronic components using conductive traces etched from copper foils laminated onto an insulating polymeric substrate. Due to high demand from the electronic industry, PCBs are produced massively. However, the waste PCBs have heavy metals and organic components which are harmful to the environment. In order to solve the pollution caused by the PCB wastes, considerable efforts have been devoted to develop recycling approaches to reuse the valuable components. Copper and other heavy metals have been successfully separated from the waste PCBs for other applications [14]. However, for the insulating polymeric substrates, the development of the relevant recycling techniques is still insufficient.

In our previous studies [15–17], we proposed an idea of recycling the polymeric substrates. Because the polymeric substrates are composed mainly of phenol formaldehyde (PF), which can provide the carbon species, they can be used as the carbon sources for the synthesis of carbon nanomaterials. As a preliminary study, we used the commercially available copper clad laminate (CCL), which is a prototype of PCB, as the test samples. Using a unique current-induced localized heating technique, the polymeric substrate, also called paper phenolic (PP) board, thermally decomposed and released some carbon-bearing species and hydrocarbon gases. With the aid of metallic catalysts (Sn and Cu), the carbon-bearing species or hydrocarbon gases were successfully transformed to the carbon nanomaterials. In the present study, the PP board was also used as the carbon source but a synthesis technique that was different from the abovementioned current-induced localized heating technique was employed. Additionally, a different catalyst (Ni) was used. Proper amounts of the PP board together with the

* Corresponding author. Tel.: +886 4 22859458; fax: +886 4 22854734.
E-mail addresses: chencm@nchu.edu.tw, chencm@dragon.nchu.edu.tw (C.-M. Chen).

0254-0584/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2011.02.030

$NiCl_2$ aqueous solution, which was used as the catalytic precursor, were thermally treated in a tube furnace. Effects of the synthesis temperature on the formation of the carbon nanomaterials were investigated.

2. Experimental methods

Fig. 1 shows a commercial CCL (Kinsten Industrial Corp., Taiwan). It is made by laminating a Cu layer (thickness: 35 μm) onto an insulating PP board, as shown in Fig. 1(a). Pretreatment was performed by immersing the CCL in an etching solution composed of H_2O_2, CH_3COOH, and H_2O (volumetric ratio = 1:1:20) to remove the surface Cu layer. The residual PP board, as shown in Fig. 1(c), was then cleaned with acetone and deionized water. A small piece was cut from the PP board and was placed in a quartz boat as the carbon source. Proper amounts of $NiCl_2$ aqueous solution (0.05–0.1 M) were poured into the quartz boat as the catalyst precursor. The $NiCl_2$ aqueous solution, which can release the Ni nanoparticles as the catalyst at moderate temperatures, has been successfully used as the catalyst precursor [18,19]. Then, the quartz boat was placed in a tubular furnace. The synthesis temperatures were set at 800, 900, and 1000 °C and the ramping rate to the synthesis temperatures was 20 °C min^{-1}. After reaching the synthesis temperature, the furnace was kept at the synthesis temperature for 1 h. To control the synthesis atmosphere, the furnace was filled with nitrogen. Filling nitrogen can remove other gases (oxygen, carbon dioxide, etc.) from the furnace, which can make sure that the PP board is the only carbon source. Additionally, the removal of oxygen can avoid the oxidation of Ni catalyst. It is important because oxidized Ni particles are nearly inactive for catalysis.

After thermal treatment, the furnace was cooled naturally to room temperature. The synthesized carbon nanomaterials were collected from the black deposits on

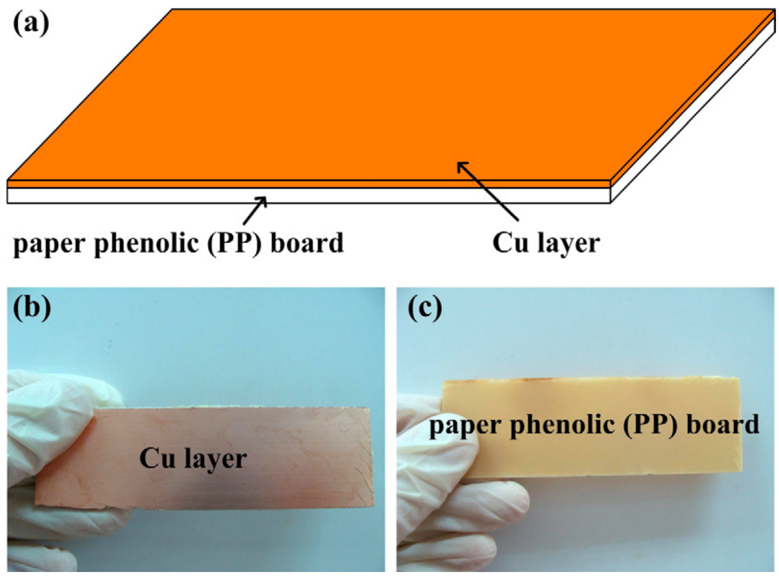

Fig. 1. A commercial CCL: (a) a schematic diagram showing that the CCL is a Cu layer laminated on a PP board, (b) a top-view image of a real sample, and (c) a top-view image of a real sample with the surface Cu layer being etched away.

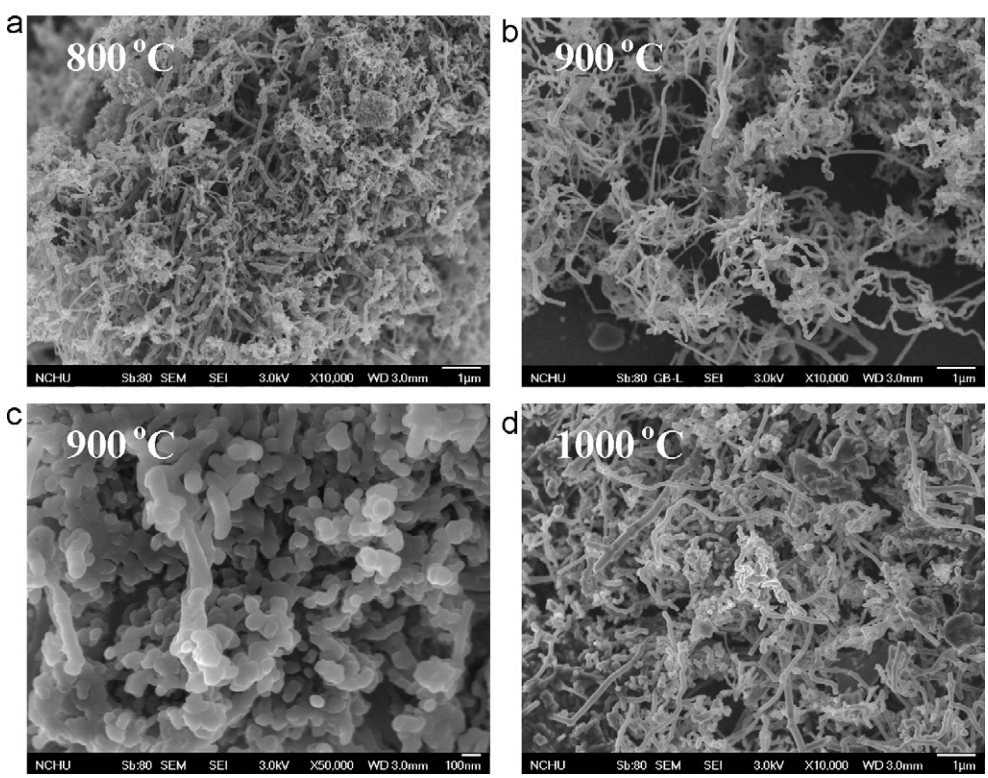

Fig. 2. SEM images of the carbon nanomaterials synthesized at (a) 800, (b) and (c) 900, and (d) 1000 °C.