Synthetic Metals 161 (2011) 1590–1595

Contents lists available at ScienceDirect

Synthetic Metals

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

Synthesis and conductivity measurement of carbon spheres by catalytic CVD using non-magnetic metal complexes

Chien-Ming Lei[a], Wei-Li Yuan[b], Hsin-Chen Huang[a], Shao-Wei Ho[c], Chi-Jung Su[c,d,*]

[a] Department of Chemical & Materials Engineering and Graduate Institute of Nanomaterials, Chinese Culture University, 55, Huagang Rd., Shilin Dist., Taipei 11114, Taiwan, ROC
[b] Department of Chemical Engineering, Feng Chia University, 100, Wenhua Rd., Xitun Dist., Taichung 40724, Taiwan, ROC
[c] School of Applied Chemistry, Chung Shan Medical University No. 110, Sec. 1, Jianguo N. Rd., Taichung 40201, Taiwan, ROC
[d] Department of Medical Research, Chung Shan Medical University Hospital, No. 110, Sec. 1, Jianguo N. Rd., Taichung 40201, Taiwan, ROC

ARTICLE INFO

Article history:
Received 2 February 2011
Received in revised form 6 May 2011
Accepted 18 May 2011
Available online 15 June 2011

Keywords:
Carbon spheres
Catalytic chemical vapor deposition
Non-magnetic metal complexes
Conductivity

ABSTRACT

Carbon spheres (CSs) have been an important subject of research in recent years. Catalytic chemical vapor deposition (CCVD) was carried out in this work to synthesize solid-core CSs at mild temperatures from 720 to 810 °C. Non-magnetic metal complexes of La, Nb, and Ti, dispersed on porous kaolin support, were tried out as catalyst. X-ray diffraction patterns revealed the graphitic structures of CSs. TEM analysis showed no encapsulated transition-metal nanoparticles inside the CSs. It was found by Raman spectra that the La catalyst resulted in CSs with higher graphitization. To examine the potential applications of CSs to the fields such as catalysis, electrochemistry, and electronic device, values of the thermal and electrical conductivity of the prepared CSs using different catalysts were measured and found to be comparable to those of the commercial carbon black.

1. Introduction

Novel carbon-based nanomaterials such as carbon spheres (CSs), carbon nanotubes, and carbon nanofibers have been attracting researchers from various disciplines to study their exciting chemical, physical, and mechanical properties [1–8]. CSs from nano- to micro-meters in size are becoming important due to their potential applications, like carbon black and nanotube, in many fields such as electro-conductive coatings, dye-sensitized solar cells, catalyst supports for impregnation of metal nanoclusters, electrochemical capacitors, battery anodes, and elements for electrostatic charge dissipation or electrical heating [9–15]. Recently, hollow spheres of metal oxides such as SiO_2, TiO_2, and SnO_2, prepared using nano/micro-sized carbon spheres as template have also been reported, which further extends the applicability of CSs [16–18].

Carbonaceous nanomaterials are frequently prepared by physical vapor deposition, electrical arc-discharge, and laser vaporization [19–22]. Chemical vapor deposition (CVD) involves carbonization of organic materials through a pyrolytic process at high temperatures above 1000 °C [23,24]. Also popular, the catalytic CVD (CCVD) is a catalyzed carbonization process which often uses transition-metal complexes of Fe, Ni, or Co to convert hydrocarbons such as methane, ethane, acetylene (C_2H_2), and carbon monoxide into carbon spheres, tubes, or fibers at a temperature well below 1000 °C [25–31]. The transition-metal nanoparticles are then derived from the metal complex precursors and sometimes found encapsulated by the carbonized material, judging from the sample's ferrimagnetism or TEM images [32]. In most cases though, the metal nanoparticles are found trapped within carbon nanotubes but separate from the CSs [24,32–35].

In the present study, we report the fabrication of nano/micro-carbon spheres by CCVD with non-magnetic complexes of La, Nb, and Ti as catalyst supported by kaolin. The microstructures of CSs were characterized by powder XRD, SEM, and TEM. The magnetic properties of CSs were tested by measuring the magnetic susceptibility at different temperatures. One advantage of using La, Nb, or Ti metal complex as catalyst is the potential for adding superconductivity to CSs if the non-magnetic metal is encapsulated within. In addition, the thermal and electrical conductivity of the CSs prepared via different catalysts were measured and compared with those of the commercial carbon black.

2. Experimental

2.1. Catalysts for CSs

To prepare the kaolin support, the kaolin powder (from Showa) was dissolved in distilled water in a weight ratio of 1:1 and stirred

* Corresponding author at: School of Applied Chemistry, Chung Shan Medical University No. 110, Sec. 1, Jianguo N. Rd., Taichung 40201, Taiwan, ROC.
Fax: +886 4 24510890.
E-mail address: suru@csmu.edu.tw (C.-J. Su).

0379-6779/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.synthmet.2011.05.023

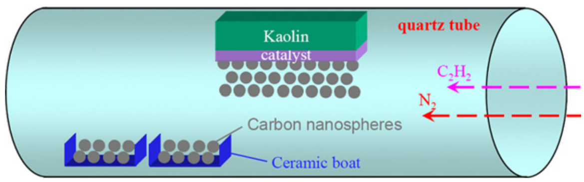

Fig. 1. Experimental setup for synthesizing carbon spheres.

for 30 min. The kaolin solution was then poured into a mold to dry up in oven at 50 °C overnight. The kaolin chunk was then carved into a boat with a trough.

To prepare the catalysts, metal complexes such as lanthanum(III) nitrate hexahydrate (from Strem), ammonium hexafluoroniobate(V) (from Acros), and titanium(IV) (triethanolaminato)isopropoxide solution (80 wt.% in 2-propanol, from Aldrich) were purchased and used as received. Firstly 1 g lanthanum (III) nitrate hexahydrate was dissolved in 5 ml distilled water and stirred for 1 h at room temperature. Next, the well-mixed solution was dripped onto a kaolin boat and dried in oven at 50 °C overnight. The drying process helps the metal complex catalyst adsorb strongly to the kaolin support. The same procedures were repeated to prepare the rest catalysts by dripping ammonium hexafluoroniobate (V) and titanium (IV) (triethanolaminato) isopropoxide on kaolin.

2.2. CCVD for CSs

The CCVD schematic for synthesizing CSs is shown in Fig. 1. The kaolin boat with catalyst was placed upside down at the center of the quartz tube in an electrical furnace. The boat was firstly heated in N_2 at 17 sccm from room temperature to 650 °C in 1 h. Next a second stream of C_2H_2 at 70 sccm was introduced into the reactor. After injection of the carbon source the temperature was further raised to the desired reaction temperature, 720 or 810 °C, in 10 min. The reaction proceeded for 1 h at the reached temperature. In the end the reactor was cooled down to room temperature by continuous flushing of nitrogen.

The CSs as fine black powder were collected by ceramic boats placed beneath the inverted catalyzing kaolin boat. Same schematic was used for all the three transition metal catalysts. The names of the CSs produced using different catalysts of lanthanum, niobium, and titanium are abbreviated as CS-La, CS-Nb, and CS-Ti, respectively.

2.3. Analyses for CSs

SEM images of the synthesized CSs were taken by JEOL JSM 5200, while the TEM ones by JEOL II 1200EX. X-ray diffraction patterns of the sample powder were acquired by Bruker MXP3. Raman spectra were scanned by Jobin-Yvon T64000. Plots of magnetic susceptibility against temperature were obtained with Quantum Design PPMS-7.

The thermal conductivity (κ) of CSs was measured in a way similar to standard methods such as ASTM E1225-09 [36]. A simple system was set up with the sample sandwiched between two copper rods and enclosed in a heat insulating container. By flowing heat through the sample, κ can be calculated using the given dimensions of the sample, temperature difference across the sample, and the heat flowrate. The system was calibrated by standard samples with known κ before testing the samples of interest.

To calculate the electrical conductivity (σ), the electrical conductance was measured first by tightly screwing the sample inside a PMMA tube and ramping a bias voltage across the sample to obtain the current–voltage (*I*–*V*) curve of which the slope was the conductance. Using the known dimensions of the sample plus the measured electrical conductance, σ can be calculated from the relation σ = (conductance) (length)/(cross-sectional area). The PMMA tube connected with an electrical multimeter (Keithley 6430, USA) was calibrated by standard samples with known σ before testing the target samples. The commercial carbon black (Vulcan XC72 from Cabot, USA) was taken as the control sample. Its thermal and electrical conductivity were measured using the same methods and compared to the samples of concern.

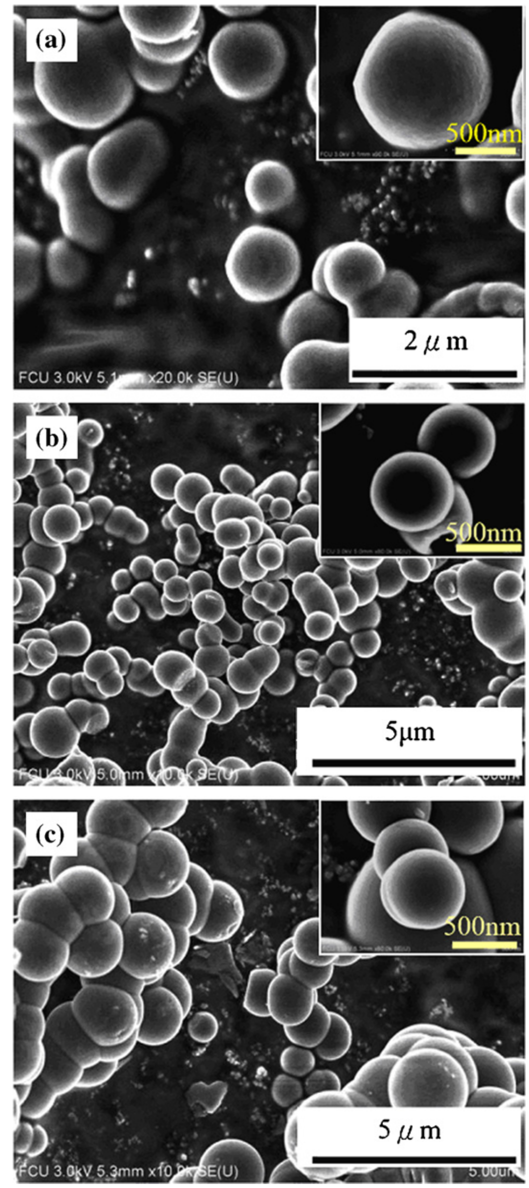

Fig. 2. SEM micrographs of (a) CS-La, (b) CS-Nb, and (c) CS-Ti; all synthesized at 720 °C. The insets are enlarged portions.

3. Results and discussion

3.1. SEM analysis

The SEM images of CSs, grown at 720 °C on kaolin support with catalytic Ti, La, and Nb metal complexes, are shown in Fig. 2. The CSs observed in Fig. 2(a)–(c) resulted from catalyzed carbonization of C_2H_2 by the metal complexes. Fig. 2(a) and (b) shows that