Diamond & Related Materials 20 (2011) 343–350

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Fabrication of CNTs with controlled diameters and their applications as electrocatalyst supports for DMFC☆

An-Ya Lo [a,b], Ningya Yu [a,1], Shing-Jong Huang [c], Chin-Te Hung [a], Shou-Heng Liu [a,2], Zhibin Lei [a,3], Cheng-Tzu Kuo [d,*], Shang-Bin Liu [a,e,**]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan
[b] Department of Material Science and Engineering, National Chiao Tung University, Hsingchu 30010, Taiwan
[c] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan
[d] Institute of Materials and System Engineering, Ming Dao University, Changhua 52345, Taiwan
[e] Department of Chemistry, National Taiwan Normal University, Taipei 11677, Taiwan

ARTICLE INFO

Available online 19 January 2011

Keywords:
Carbon nanotube
Templating synthesis
Chemical vapor deposition
Hexagonal mesoporous silica
Electrocatalyst
Direct methanol fuel cell

ABSTRACT

A facile synthesis procedure based on chemical vapor deposition (CVD) process has been developed to fabricate carbon nanotubes (CNTs) with controlled diameters and high yields utilizing Fe-containing ordered hexagonal mesoporous silicas (HMSs) such as MCM-41 and SBA-15 having varied pore sizes as the catalysts as well as the templates. It is found that unlike Fe/HMS catalysts prepared by co-precipitation method, samples prepared by the impregnation method gave rise to multi-wall CNTs with uniform diameters, which were largely dictated by the pore size of the Fe/HMS catalysts. Among these uniform MWCNTs, sample with a larger diameter (≥8 nm) was found to be more favorable as support for Pt catalyst, leading to a homogeneous dispersion of metal nanoparticles. Consequently, the Pt/CNT electrocatalysts so prepared gave rise to superior methanol oxidation activities as well as tolerances for CO poisoning compared to Pt supported on commercial single-wall CNT (Pt/SWCNT) and XC-72 activated carbon (Pt/XC-72) having a similar metal loading.

1. Introduction

Recent developments in fabrication of porous carbon supports with high surface areas and controllable morphologies have received considerable attention in R&D of supported electrocatalysts for direct methanol fuel cells (DMFCs) and proton-exchange membrane fuel cells (PEMFCs), which have been considered as the most prominent candidates for next-generation portable power sources [1–4]. Highly dispersed noble metal (Pt, Ru) nanoparticles (NPs) supported on conductive materials with high surface areas, such as carbon blacks [5,6], ordered mesoporous carbons (OMCs) [7–13], and carbon nanotubes (CNTs) [14–18], are pertinent anodic/cathodic electrocatalysts for DMFCs and PEMFCs. Among them, CNTs have received considerable attention due to their unique one-dimensional nanostructure and superior electrical conductivity. Aside from the most common electrocatalysts for DMFCs, such as Pt/Ru supported on commercial Vulcan XC-72 carbon black, many attempts have been made utilizing CNTs as catalyst supports [14–23]. However, while majority of past research efforts have been devoted in optimizing the metal dispersion on single-wall (SW) and multi-wall (MW) CNTs aiming to promote their electrocatalytic performances and durability, practically no report had been focused on the diameter size of the CNT supports.

In general, the methodologies invoked in controlling the diameter of CNTs during chemical vapor deposition (CVD) process may be classified into two main categories, namely by controlling the processing parameters and by employing an auxiliary template. For the former, it has been reported that parameters such as the carrier gas/carbon source flow rate, plasma intensity, morphology of the catalyst, precursor compositions, and duration of treatment etc. have considerable effects on the diameter of the final CNT products [24–28]. In contrast to such sophisticated adjustment of processing parameters, the use of an auxiliary template appears to be more advantageous in fabricating CNTs with tailorable diameters. For examples, zeolites [29] and anodic metal oxides [30–36] have been utilized as hard templates during the CVD process to fabricate CNTs with uniform diameters. In this case, the diameters of the CNTs so synthesized are largely dictated by the pore size of template used. However, since it is rather difficult to prepare anodic metal oxides

☆ Presented at NDNC 2010, the 4th International Conference on New Diamond and Nano Carbons, Suzhou, China.

* Corresponding author. Fax: +886 4 8879050.
** Correspondence to: S.-B. Liu, Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan. Fax: +886 2 23620200.
E-mail addresses: kuoct@mdu.edu.tw (C.-T. Kuo), sbliu@sinica.edu.tw (S.-B. Liu).
[1] Present address: Institute of Fine Catalysis and Synthesis and Key Lab of Sustainable Resources Processing and Advanced Materials of Hunan Province, Hunan Normal University, Changsha 410081, China.
[2] Present address: Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung 80778, Taiwan.
[3] Present address: Department of Chemical & Biomolecular Engineering, National University of Singapore, Singapore.

0925-9635/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2011.01.002

with uniform pore sizes less than 25 nm, majority of the CNTs so fabricated possess diameters exceeding 25 nm [36]. On the other hand, CNTs fabricated by using microporous zeolites as templates mostly have diameters less than 1 nm. In view of the fact that the diameter of CNT is one of the key parameters affecting their physical properties, it is highly desirable to develop a facile synthesis route to fabricate CNTs with tunable diameters within the range of 1–25 nm.

Ordered hexagonal mesoporous silicas (HMSs), especially those possessing straight mesoporous channels with uniform pore sizes in the range of 2–50 nm, such as MCM-41 [37] and SBA-15 [38,39] seem to represent the ideal templates to meet the aforementioned demand [40]. It is worth mentioning that although various ordered mesoporous silicas have been invoked for the preparation of CNTs, they were mostly employed as supports to disperse or to limit the size and structure of the catalytic metal nanoparticles [41–48], overlooking the templating function of the porous substrates. We report herein a facile synthesis route to synthesize CNTs with tunable diameters and high yields by using Fe-containing HMSs as catalyst templates. The resultant CNTs with varied diameters were used as supports to prepare various Pt/CNT anodic electrocatalysts for DMFC applications and their catalytic performances during methanol oxidation reaction (MOR) were evaluated and compared with a Pt/XC-72 catalyst (12.5 wt.% Pt on Vulcan XC-72).

2. Experimental

2.1. Preparation of Fe-containing HMSs

Three types of ordered HMSs, namely MCM-41, SBA-15, and pore expanded SBA-15 (denoted as PE-SBA-15) were synthesized by known recipes reported previously [37–39,49]. Iron catalyst was loaded onto the HMSs *via* either co-precipitation or impregnation methods. For the former, typically ca. 0.4 g of $Fe(NO_3)_3$ was stirring with 1.0 g of the target HMS material for 0.5 h in deionized water (20 mL), followed by filtering and drying at 373 K, then subjected to reduction treatment under H_2 at 773 K for 3 h. The Fe-containing HMSs so obtained from the siliceous MCM-41 and SBA-15 are denoted as Fe(co)/MCM-41 and Fe(co)/SBA-15, respectively. In the case of loading Fe catalyst by the impregnation method, proper amount of Fe $(NO_3)_3$ (ca. one-half pore volume of the corresponding support) was dissolved in 20 mL deionized water, followed by adding 1.0 g of the target HMS. After being stirred for 0.5 h, the suspension was dried under vacuum. The obtained product was further stirred in presence of dichloromethane (CH_2Cl_2) to facilitate migration of Fe precursors into the hydrophilic channels of the HMSs [50], followed by removal of the CH_2Cl_2 solvent by evacuation. The above procedure was repeated once and the final product was subjected to reduction treatment carried out by first slowly ramping (2 K/min) the temperature to 373 K under dried Ar, kept at the same temperature for 3 h, followed by reduction under H_2 environment before a mixture of acetylene (C_2H_2) and hydrogen (H_2) was injected for CNTs growth. The Fe-containing HMSs so derived from the siliceous MCM-41, SBA-15, and PE-SBA-15 are denoted as Fe(im)/MCM-41, Fe(im)/SBA-15, and Fe(im)/PE-SBA-15, respectively.

2.2. Fabrication of CNTs with uniform diameters

CNTs with varied diameters were prepared by a CVD method similar to that reported earlier for the nano-sized tubular carbons (i.e., CMTs) [51]. In brief, the syntheses were carried out in a home-made quartz reactor using various Fe-containing HMSs as templates. Typically, after loading ca. 0.5 g of the fresh Fe-containing HMS in the reactor, the system was first gradually heated (1 K/min) to 873 K under vacuum, followed by injecting a stream of C_2H_2/H_2 gas mixture at a flow rate of 50/50 sccm/sccm for 40 min under a pressure of *ca.* 2 kPa. The resultant product was stirred with excess aqueous HF solution (1 M, 50% ethonal–50% H_2O) for 24 h to remove the silica template and Fe species, followed by filtering and drying under vacuum to obtain the final multi-wall carbon nanotube (MWCNT) materials.

2.3. Preparation of Pt/CNT electrocatalysts

To explore the effect of tube diameter on the performances of various CNTs as catalyst supports for DMFC at anode, typically ca. 0.2 g of the selected home-made CNT was individually suspended in 10 mL of H_2PtCl_6 aqueous solution (0.04 M) at room temperature. After removing water under reduced pressure, the obtained solid was treated at 523 K for 0.5 h under H_2 atmosphere to provoke reduction

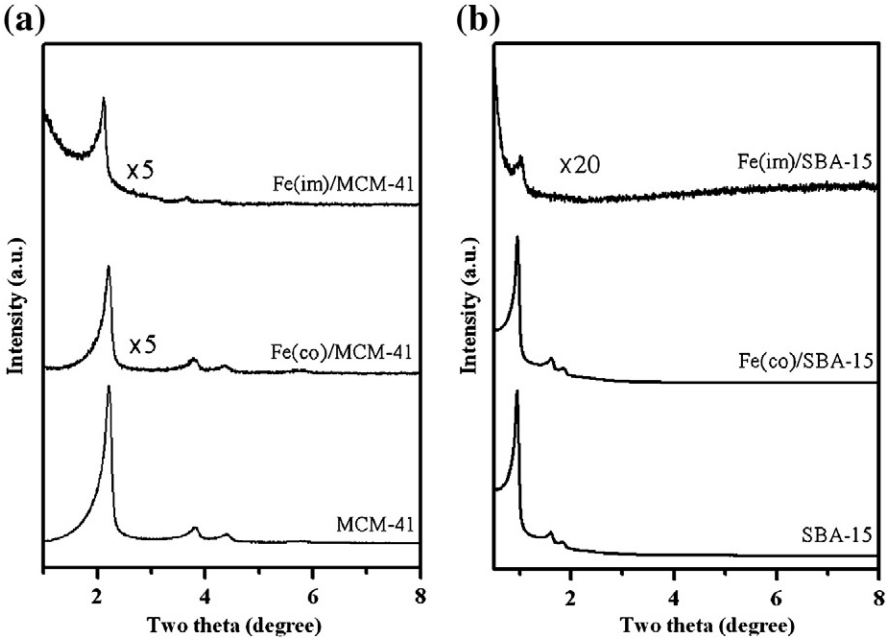

Fig. 1. Small-angle XRD patterns of siliceous and Fe-containing HMSs; (a) MCM-41 and (b) SBA-15.