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TEM investigation on the initial stage growth of carbon onions synthesized by CVD

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Abstract

We report an investigation on the initial stages of growth of carbon onions synthesized by CVD of methane. A special experimental procedure has been developed to stop the process after short duration (10 s–2 min). It has found that during the early stages (90 s), carbon atom cluster encapsulated nanoparticles were formed. With increasing synthesis time (2 min), the carbon clusters began to graphitize to form graphitic layers. High resolution transmission electron microscope observations showed that many catalytic particles were partially encapsulated with graphitic layers, which were responsible for the hollow carbon onion formation.

Keywords: Carbon onions; Chemical vapor deposition; Transmission electron microscopy

1. Introduction

Carbon onions, which are quasi-spherical carbon nanoparticles consisting of concentric graphitic shells, are expected to be a new conformation of nanosize carbon materials and have good prospects for several applications of composite materials, magnetic storage media and wear-resistant materials [1,2]. Since the first observation of carbon onions [2], many attempts have been made to fabricate these onions and understand their formation mechanism [3,4]. Iijima [2] once tried to describe this new structure with a model involving a mixed sp^2/sp^3 hybridization of carbon atoms. However, the scientific community did not pay much attention to this explanation before the fullerene one [5] and it is only in 1987 [6,7] that the structures characterized by Iijima were reconsidered and discussed in terms of fullerene structures. Actually, the intense interest devoted to the carbon onions was in 1992, when Ugarte [8] discovered a reproducible technique to realize their formation that consists in irradiating carbon soot by an intense electron beam in a transmission electron microscope (TEM). Except for this production technique, several other methods were also developed to synthesize carbon onions. Thermal treatment of fullerene black [9], shock-wave treatment of carbon soots [10], dc arc-discharge of graphite electrode [11], pulsed laser deposition [4], and catalytic decomposition of carbon containing gases [12,13] at elevated temperatures appears as the most promising technique for producing numerous carbon onions with high purity.

Previously, we have obtained a mass of carbon onions in the process of catalytic decomposition of methane over Ni/Al catalyst at low temperature [12]. Compared with above carbon onion synthesis method [4,9–11], our carbon onions synthesized were in large quality and with diameters ranging from 5 to 50 nm, and that the synthesis equipment was relatively inexpensive. We have since paid much attention to this kind of carbon nanostructure. Because a thorough understanding of the formation mechanism for such carbon nanostructure is crucial to design procedures for controlling the growth conditions in order to obtain structures which might be directly used in different fields in nanotechnology, and that some models describing the formation of nano-onions fabricated by the methods including electric arc, high-energy electron irradiation of carbonaceous materials, and thermal treatment of "fullerene black" have been suggested in Refs. [14–17]. However, the growth mechanism of carbon onions by CVD is still under discussion. Therefore, the understanding of carbon onion formation during the initial stages of the growth is of particular importance. To the best of our knowledge, no experimental study of the initial stages of carbon onion growth by CVD of methane is reported.

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In this study, we report an investigation on the initial stages of the carbon onion growth performed to understand the mechanism operating in the formation of nano-onions. We developed a specific synthesis procedure in order to control precisely the synthesis duration for short times. A particular interest was devoted to the study of the location of catalyst particles and their chemical nature, morphology and size distribution when nano-onions started to grow in order to get information related to their growth mechanism. The understanding of the parameters involved would allow the development of efficient production procedures.

2. Experimental

The fabrication procedures of catalyst are similar to those described in Ref. [12]. In brief, the right amounts of $Ni(NO_3)_2{\cdot}6H_2O$ and aluminum powder were mixed in 1 l distilled water to yield the final weight ratio of Ni/Al equal to 3/1, and appropriate NaOH dissolved in 50 ml distilled water was added to the previous mixture with constant stirring. The colloid obtained was then washed for several times with distilled water and dried in a vacuum furnace. Finally, the colloid was calcined in N_2 atmosphere at 400 °C for 4 h to form fine NiO/Al composite powder, which was employed in the following carbon onion synthesis experiment.

In the catalytic decomposition processes, some catalyst of the NiO/Al was put in a quartz boat and placed in a horizontal quartz tube reactor. In order to convert the nickel oxides in the catalyst to metallic Ni, the catalyst was firstly reduced at 600 °C in a hydrogen atmosphere for 2 h. Then, carbon onions were grown at 600 or 550 °C for some time (10 s–2 min) by introducing a mixture of CH_4/N_2 into the reactor at a flow rate of 60 ml/min/420 ml/min. Then the gas flow was switched back to nitrogen with a very large flow rate (2000 ml/min) after the growth process to purge the methane from the tube in short order and to prevent back flow of air into the tube. The furnace was then allowed to cool to room temperature before exposing the carbon nanomaterials to the air.

A small quantity of the as-prepared carbon nanomaterials has been dispersed in ethanol and dispersed onto copper grids in order to perform detailed observations on individual nano-onion by transmission electron microscopy (TEM) and high resolution TEM (HRTEM) (Philips Tecnai G^2 F20, 200 kV). Energy-dispersive X-ray (EDX) analyses were coupled to TEM observations to determine the nature of the products.

3. Results and discussion

TEM images (Fig. 1) show the changes in the morphology of the products when varying the synthesis duration from 10 s to 2 min, for 600 °C catalytic decomposition temperature. For duration of 10 s (Fig. 1a and b) and 20 s, essentially few things

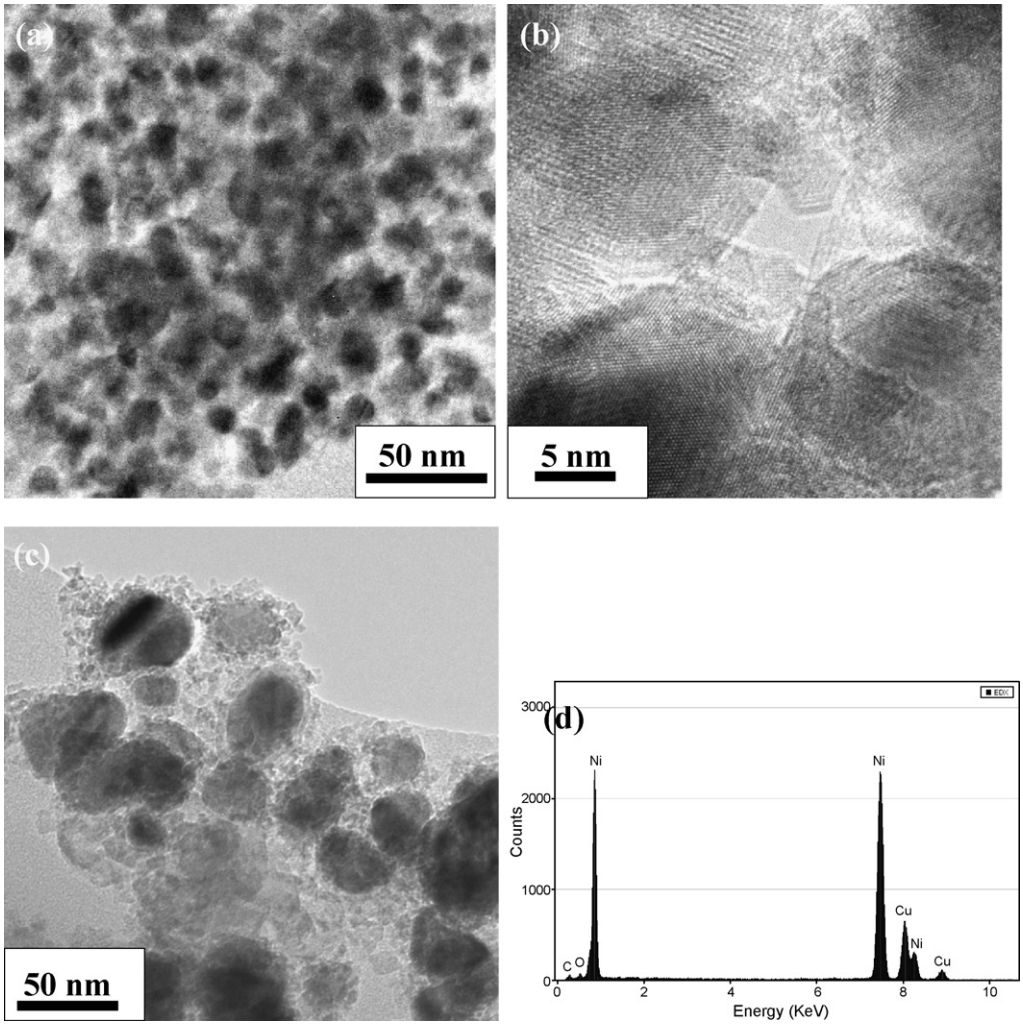

Fig. 1. (a) TEM and (b) HRTEM image of the early stages of nano-onion growth for 10 s at 600 °C from catalytic decomposition of methane. (c) TEM image of the early stages of nano-onion growth for 2 min at 600 °C from catalytic decomposition of methane; this image reveals catalytic particles encapsulated by carbon atom clusters. (d) EDX analysis of catalytic particle encapsulated by carbon atom clusters (600 °C, 2 min).