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Environmental transmission electron microscopy investigations of Pt-Fe_2O_3 nanoparticles for nucleating carbon nanotubes

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ABSTRACT

Elucidating the evolution of bimetallic catalyst for nucleating carbon nanotube has been challenging. In this work, acorn-like Pt-Fe_2O_3 nanoparticles are developed for the growth of single-walled carbon nanotubes (SWCNTs) by chemical vapor deposition. Using *in situ* environmental transmission electron microscopy, restructuring of the acorn-like Pt-Fe_2O_3 nanoparticles at reaction conditions is investigated. Upon heating to reaction temperature, ε-Fe_2O_3 is converted to β-Fe_2O_3, which can be subsequently reduced to metallic Fe once introducing CO. As Pt promotes the carburization of Fe, part of the metallic Fe reacts with active carbon atoms to form $Fe_{2.5}C$ instead of Fe_3C, catalyzing the nucleation of carbon nanotubes. Nanobeam electron diffraction characterizations on SWCNTs grown under ambient pressure at 800 °C demonstrate that their chiral angle and diameter distributions are similar to those of SWCNTs grown on monometallic Fe. The results further indicate that the active components in both the catalysts, determining the chirality distribution of SWCNTs, are similar. In addition, Pt facilitates the reduction of Fe_2O_3, rendering SWCNT growth at a relatively low temperature of 700 °C. This work provides a profound understanding of the structural reconstruction in bimetallic catalyst, shedding more light on designing novel catalysts for the growth of SWCNTs.

1. Introduction

Since the landmark work on the synthesis of single-walled carbon nanotubes (SWCNTs) by electric arc technique using Fe-containing cathode [1], the search for better catalysts has been one of the main tasks in controlled synthesis of SWCNTs. Of numerous catalysts studied, bimetallic catalysts have attracted particular interests due to their high activity and better control over SWCNT structures by chemical vapor deposition (CVD) technique. As the result of adding a second metal, catalysts, such as CoMo [2], CuFe [3], RuFe [4], PtCo [5] and WCo [6,7], lead to higher carbon nanotube yields and narrower chirality distributions compared to their monometallic counterparts. In spite of these progresses, secret behinds the successful growth is far from being clarified. For example, a mysterious WCo bimetallic system has been reported by two research groups to selectively grow (12, 6) SWCNTs [6,7]. Yang et al. [6] proposed that the fabrication of stable W_6Co_7 alloy is responsible for the preferential synthesis of (12, 6) SWCNT. While recent work by An et al. [7] identified an intermediate structure of Co_6W_6C, where most of W atoms disappear after 5 min CVD growth, indicating the complexity in determining the active catalyst components for SWCNT synthesis.

Pt-based bimetallic particles have long been applied as excellent catalysts for generating carbonaceous deposits, such as carbon filaments and SWCNTs [5,8,9]. Pioneer work by Bark et al. [8],

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reported the formation of filaments when heating Pt–Fe particles in acetylene. It was discovered that, with the addition of Pt into Fe catalyst, the growth rate of filament increased two orders of magnitude [8]. Using PtCo catalyst, Liu et al. [5] achieved a narrow SWCNT chirality distribution at a relatively high temperature of 800 °C. Recently, Ohashi et al. [9] prepared half-buried FePt between deposited MgO for growing vertically aligned SWCNTs with metallic chirality.

Besides the achievements in carbon nanotube synthesis using Pt-based catalyst, uncovering the structure of catalyst particles under reaction conditions is of fundamental importance in understanding SWCNT nucleation mechanisms and establishing structure correlations between catalysts and SWCNTs. Although alloy formation was observed after CVD growth by *ex situ* characterizations [5,9], some works suggest that separation of the alloy components could occur under certain conditions [8,10]. In order to address the detailed structural change and track the evolution of catalyst nanoparticles, it is necessary to map the atomic structure in reactive environments using *in situ* environmental transmission electron microscopy (TEM) [11].

In the work reported here, we present an acorn-like Pt-Fe_2O_3 catalyst for the growth of carbon nanotubes. Combined with *ex situ* TEM characterizations on catalyst nanoparticles before and after CVD growth, *in situ* environmental TEM was carried out to clarify the structural dynamics of such hybrid nanoparticles in nucleating carbon nanotubes. In addition, SWCNTs grown at different temperatures will be characterized and compared with those synthesized on monometallic Fe.

2. Materials and methods

2.1. Formation of acorn-like Pt-Fe_2O_3 catalyst

Similar to the previously reported Fe–Ti–O catalyst [12], the Pt-Fe_2O_3 catalyst was prepared by combining Pt layer deposition onto premade Fe nanoparticles with subsequent high-temperature air calcination. Briefly, FeO_x nanoparticles generated by hydrolysis of ferric chloride [13] were first casted onto Si_3N_4 TEM grids, a thin layer of Pt was then sputtered onto the grids with a current of 10 mA for 1 min in an Emitech K100X glow discharge unit. The catalyst was finally annealed at 800 °C for 20 h in a muffle furnace.

2.2. Growth of carbon nanotube with Pt-Fe_2O_3 catalyst

Carbon nanotubes were grown by CVD. Pt-Fe_2O_3 catalyst supported by Si_3N_4 TEM grid was loaded into a horizontal CVD reactor followed by flushing with 200 cm^3/min helium. After reaching the desired temperature, CO with a flow rate of 200 cm^3/min was introduced to the CVD reactor, in place of helium stream. CO was turned off after 1 h and the CVD reactor was cooled under helium environment.

2.3. Characterizations of Pt-Fe_2O_3 catalyst and carbon nanotubes

TEM observations of Pt-Fe_2O_3 nanoparticles were carried out on a JEOL-2200FS TEM and a Zeiss LIBRA 200FMC TEM. Elemental analysis was performed by energy dispersive X-ray (EDX) spectroscopy and electron energy-loss spectroscopy (EELS). The structure and morphology of carbon nanotubes were studied by a JEOL-2200FS TEM operated at 80 kV. Electron diffraction patterns of randomly distributed carbon nanotubes were taken to determine the chirality and diameter distributions of carbon nanotubes.

2.4. In situ environmental TEM studies on dynamics of Pt-Fe_2O_3 catalyst and nucleation of carbon nanotube

Pt-Fe_2O_3 catalyst supported by a Si_3N_4 TEM grid was mounted in a Gatan heating holder, which was then inserted in an FEI Titan 80-300ST environmental TEM and heated to 700 °C in vacuum. Subsequently, a flow of CO (6 cm^3/min) was introduced into the TEM chamber to stabilize at a pressure of 8 mbar. The structural evolution of the catalyst particles was monitored in real time during the chemical reaction at 300 kV.

3. Results and discussion

3.1. Characterizations of Pt-Fe_2O_3 catalyst before and after CVD growth

ESI Fig. S1a presents a TEM close view image of nanoparticles prepared by Pt deposition onto iron oxide nanoparticles followed by high temperature calcination. A detailed examination shows that the acorn-like particles consist of a dark embryo partly enclosed by a light cupule. On the basis of the TEM image (Fig. 1a) and its corresponding fast Fourier transform (FFT) pattern (Fig. 1b), the dark embryo can be well assigned as face centered cubic (FCC) structured Pt with a lattice parameter of 0.393 nm (pdf card: 04-0802). The lattice spacing measured from the TEM image is 0.23 nm (Fig. 1a), resembling its (111) plane spacing (0.227 nm). Similarly, the cupule in light contrast is indexed as orthorhombic Fe_2O_3 (a = 0.509 nm, b = 0.878 nm, c = 0.943 nm, pdf card: 52-1449) based on the structural analysis of particle shown in Fig. 1c and its FFT pattern (Fig. 1d).

In addition, moiré pattern is observed in Fig. 1c, suggesting that at least part of Pt is covered by Fe_2O_3 layer. Such an assignment is further confirmed by EELS on the hybrid nanoparticles. As shown in Supporting Information Fig. S1b, the EELS spectrum from the cupule part exhibits the L_3 and L_2 peaks of Fe at 710 eV and 722 eV,

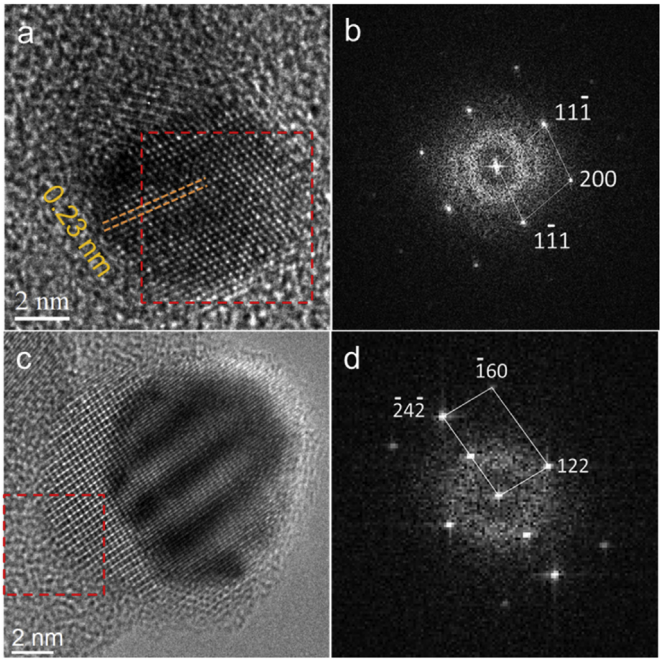

Fig. 1. (a) A high resolution TEM image of an acorn-like Pt-Fe_2O_3 hybrid nanoparticle and (b) the FFT pattern of the dark part of the hybrid structure. (c) A high resolution TEM image of another Pt– Fe_2O_3 hybrid nanoparticle and (d) the FFT pattern of the square part of the particle. (A colour version of this figure can be viewed online.)