# Interpretation of Ostwald ripening of catalytic nanoparticles based on the radial breathing mode in single-walled carbon nanotubes

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HIGHLIGHTS

- Ostwald ripening of catalytic nanoparticles for single-walled carbon nanotubes was explored.
- The density of the nanoparticles was adjusted by varying the spin-coating conditions.
- This density control affects the determination of the diameter distribution and tube type.
- Diameter-selective growth of single-walled carbon nanotubes was successfully achieved.

ABSTRACT

Catalytic nanoparticle (NP) size is the crucial factor that determines carbon nanotube (CNT) diameter. Therefore, we explored the Ostwald ripening phenomenon of catalytic NPs from the radial breathing modes in resonant Raman spectra of synthesized single-walled CNTs (SWCNTs). SWCNTs were synthesized using chemically derived monodisperse Fe oxide catalytic NPs by a conventional thermal chemical vapor deposition system. The density of the NPs was manipulated by simply adjusting the spin-coating speed and cycle. The diameter distribution and tube type (SWCNTs or multi-walled CNTs) were thereby determined, which can be understood by density-dependent Ostwald ripening of the NPs. As a result, the diameter-selective growth of SWCNTs was successfully achieved, which will be useful for SWCNTs-based electronic applications.

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## 1. Introduction

Single-walled carbon nanotubes (SWCNTs) have gained much interest in a variety of applications due to their extraordinary electrical properties that originate from their quasi one-dimensional structure [1,2]. In particular, the electronic structures of SWCNTs are determined by their diameter and $(n, m)$ chirality, which is described as a cylindrically rolled graphene sheet [3]. In terms of the chirality, metallic SWCNTs are given by $n-m=3q$, where $q$ is an integer, whereas semiconducting SWCNTs are given by $n-m \neq 3q$, and their energy gap is inversely proportional to the diameter. Hence, the predominant synthesis of SWCNTs with uniform diameter and chirality is required for the development of high-performance SWCNTs-based nanoelectronics [4]. It is noted that the diameter and chirality of SWCNTs are determined by the size of the catalytic nanoparticles (NPs) used for chemical vapor deposition (CVD) growth [5–7]. Unfortunately, size-inhomogeneity of catalytic NPs is accelerated during SWCNTs growth. This phenomenon can be explained by Ostwald ripening, a process that causes heat-driven size-inhomogeneity of the NPs through the transfer of atoms from smaller particles to larger particles [8]. This transport of atoms can be induced by the chemical potential difference related to the size of two adjacent particles. The synthesis of SWCNTs with a broad diameter distribution inevitably occurs through these processes. Therefore, a fundamental understanding of Ostwald ripening of catalytic NPs enables us to

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obtain size-homogeneous and controllable catalytic NPs for future electronic applications based on SWCNTs.

Here, we explored the effect of densification of Fe oxide catalytic NPs on the synthesized SWCNT diameters. This correlation was understood in terms of the Ostwald ripening of the Fe oxide NPs under SWCNTs growth conditions. Precise control of SWCNT diameters was achieved by tuning the spin-coating conditions of the Fe oxide solution.

## 2. Experiments

One-nanometer-scale size-controlled monodisperse Fe oxide NPs were prepared by a previously reported method [9]. Subsequently, 2 nm-size monodisperse Fe oxide NPs dissolved in chloroform were selected for SWCNTs growth (concentration: 0.3 mg/ml). A 15 nm-thick Al layer was first deposited onto a Si(0 0 1) substrate using dc magnetron sputtering. This substrate was then annealed at 650 °C for 30 min in air to form an $Al_2O_3$/Si substrate. An $Al_2O_3$ support layer has been widely employed because of its crucial roles in preventing silicide formation and retarding surface diffusion of catalytic NPs [10]. The solution of Fe oxide NPs was spin-coated onto the $Al_2O_3$/Si substrate with rotational speeds of 2000, 3000, and 4000 rpm for 30 s. The prepared catalytic layers were placed in a thermal CVD (TCVD) reactor and were heated to 800 °C under an Ar (800 sccm) and $H_2$ (100 sccm) gas mixture. When the TCVD reactor reached the target temperature, $C_2H_2$ (50 sccm) was introduced as a carbon feedstock with the $Ar/H_2$ mixture for 10 min to synthesize the SWCNTs. The $C_2H_2$ was then turned off, and the TCVD reactor was then cooled to room temperature under the $Ar/H_2$ environment. The diameter distribution of synthesized SWCNTs was examined by resonant Raman spectroscopy (Renishaw, RM1000 inVia). Raman spectra were recorded at excitation wavelengths of 633 and 514 nm. The incident laser power focused on the samples was adjusted to be 3 mW/cm$^2$ to avoid local heating-induced structural deformation. The laser spot size is ~5 μm focused by a 100× optical lens and the spectral resolution is ~1 cm$^{-1}$. The spectra were recorded under ambient conditions. All spectra were normalized to the G-band (1591 cm$^{-1}$) and deconvoluted by a Lorentzian function. The structural and chemical properties of monodisperse Fe oxide NPs were investigated by transmission electron microscopy (TEM; JEOL, JEM2100F), atomic force microscopy (AFM; SEIKO, SPM400), and X-ray photoelectron spectroscopy (XPS; VGMICRO TECH, ESCA 2000).

## 3. Results and discussion

Monodisperse Fe oxide NPs dissolved in chloroform were dropped onto carbon coated Cu grid for TEM observation and the solvent was allowed to evaporate slowly at room temperature. Fig. 1a exhibits an HR-TEM image of chemically derived monodisperse Fe oxide NPs, in which NPs with an extremely narrow size distribution are clearly observed, and the average size is estimated to be 2.1 nm. Chemical identification of the NPs was carried out by XPS. XPS spectra were acquired with a normal emission geometry using conventional monochromatic Al $K\alpha$ (1486.6 eV) radiation. The Fe 2p core level spectrum obtained from the NPs spin-coated on the Si(0 0 1) substrate shows that the resultant positions of Fe $2p_{3/2}$ (binding energy ($E_B$)=710.9 eV) and Fe $2p_{1/2}$ ($E_B$=724.9 eV) correspond to those of Fe oxide [11], as shown in Fig. 1b. From these results, precise control of SWCNT diameter seems to be possible because uniformly-sized monodisperse Fe oxide catalytic NPs were formed. However, Ostwald ripening of the high-density NPs inevitably occurred at the SWCNT growth temperature. Densification of the NPs was manipulated by adjusting the spin-coating condition of the solution. If the interparticle distance of the NPs is longer than the lateral diffusion length at these conditions, Ostwald ripening of monodisperse Fe oxide NPs could be restricted. This phenomenon will be traced by examining the diameter distribution of the tube using resonant Raman spectroscopy.

Raman spectroscopy with excitation wavelengths of 633 and 514 nm was used to evaluate the diameter distribution of SWCNTs. Fig. 2a–c exhibit the radial breathing modes (RBM) in resonant Raman spectra of the SWCNTs synthesized using monodisperse Fe oxide NPs prepared by spin-coating at 2000, 3000, and 4000 rpm, respectively. In general, the diameter, chirality, and electrical properties of SWCNTs can be extracted from the RBM, which originates from the phonon vibrational mode of carbon atoms in the radial direction [12]. The RBM spectra were recorded from various areas under each condition, revealing excellent uniformity in terms of their diameter over large areas. The RBM peaks were observed at 195–285 cm$^{-1}$ for the SWCNTs synthesized at 2000 rpm, which indicates that the SWCNTs possess a relatively broad diameter distribution. It is interesting to note that the intensity of RBM peaks at 254 and 284 cm$^{-1}$ decreased gradually with increasing rotational speed up to 4000 rpm, whereas the peak at 195 cm$^{-1}$ was predominant, indicating the diameter-selective growth of SWCNTs. From the RBM peaks, we determined the diameter of the SWCNTs according to the equation $w$ (cm$^{-1}$)= $223.5/d$ (nm)+12.5 [13], where $w$ and $d$ denote the wavenumber
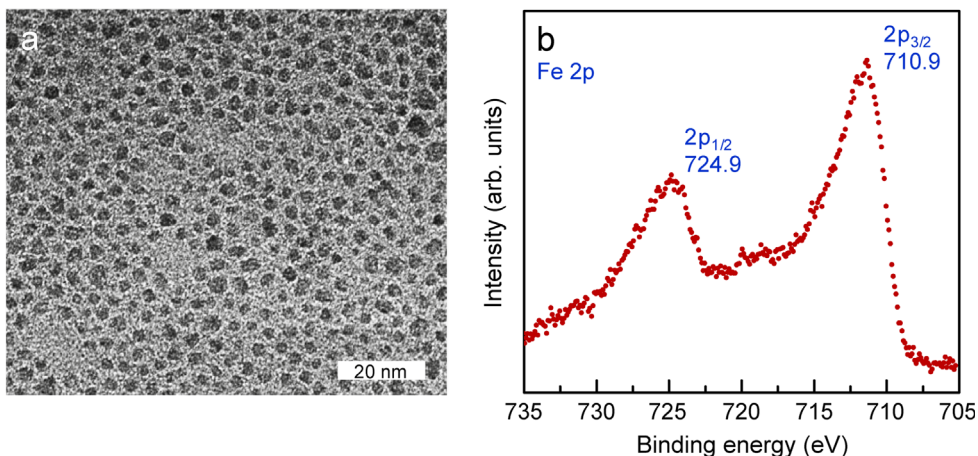


**Fig. 1.** (a) HR-TEM image and (b) the Fe 2p core level spectrum of chemically derived monodisperse Fe oxide NPs.