The growth of carbon nanostructures was performed by means of the thermal CVD technique in a tubular quartz furnace of 25 mm in diameter (Atomate Corporation, CA). The catalytic systems were reacted in C_2H_4/CH_4 mixture (1:1) at 750 °C for 30 min. Mixture of H_2/Ar (10% of H_2) was used as the carrier gas (in a ratio 10:1 to the hydrocarbon gas mixture). After thermal CVD, typical carbon microfibre segments were selected for surface characterization. The characterization was performed using a scanning electron microscope (SEM) (JEOL JSM-6490LV) at an operating voltage of 25 kV. Fig. 3A and B shows the SEM micrographs of carbon microfibres loaded with the polymer–metal complex after thermal CVD. It can be observed that the surface of the carbon microfibres has been well covered with fibrillar carbon nanostructures. The presented concept can be considered as a universal way to coat any type of catalyst on a targeted substrate for the growth of carbon nanostructures. Besides, it can be applicable for broader range of substrates with complex morphology and micro-features.

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Gadolinium and europium catalyzed growth of single-walled carbon nanotubes

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A R T I C L E I N F O

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A B S T R A C T

The inner transition metals, gadolinium (Gd) and europium (Eu) have been shown to catalyze the growth of single-walled carbon nanotubes (SWCNTs) using chemical vapor deposition. The Gd and Eu nanocatalysts, prepared using a diblock copolymer templating method and characterized by atomic force microscopy, were uniformly spaced over a large deposition area with an average diameter of 1.9 nm and narrow size distribution. Characterization by transmission electron microscopy and Raman spectroscopy confirms the presence of SWCNTs catalyzed by Gd and Eu with an average diameter of 2.05 nm.

Single-walled carbon nanotubes (SWCNTs) possess a number of interesting and unique physio-chemical properties suitable for a wide range of applications in material and biomedical sciences [1]. Understanding the synthesis/growth of SWCNTs is key to their technological development and remains a significant scientific challenge [2]. There are various techniques used for the growth of SWCNTs including arc discharge, laser ablation, and chemical vapor deposition (CVD) [3]. Among these techniques, CVD is the most powerful and versatile method allowing large scale synthesis of high quality SWCNTs. This process utilizes metal nanoparticles as catalysts to allow carbon feedstock cracking, nucleation, and...
growth of SWCNTs. The structure, length, and yield are affected not only by CVD-related parameters such as the carbon feedstock type, growth time, and temperature, but also the composition and size of the metal catalysts used for CVD. Based on the metal–carbon binary phase diagrams [2], the transition metals iron (Fe), cobalt (Co), and nickel (Ni) are considered to be the most suitable and thus widely used as catalysts for SWCNT growth. However, other transition metals and alloys have been explored as catalysts to provide insight into the growth mechanisms of SWCNTs and to control the assortment of properties that have inspired numerous studies across various fields [4–6].

To date, all the metal-catalyzed SWCNT growth studies have mainly focused on transition metals. Curiously, f-block transition elements also referred to as inner transition elements have still not been well explored. One reason could be that inner transition elements are not known to be highly catalytic as the transition elements. It has also been suggested that lanthanoids such as gadolinium (Gd) and europium (Eu) exhibit insufficient carbon solubility, slow carbon diffusion, and limited carbide formation to catalyze SWCNT growth [2]. Towards the goal of systematically examining the efficacy of inner transition metals, particularly lanthanoids, to facilitate SWCNT growth, we report the first demonstration of a CVD-based technique that allows the growth of SWCNTs using Gd and Eu.

The method of SWCNT synthesis involves CVD of carbon feedstock on metal catalysts prepared by a diblock copolymer templating technique (For experimental details please see Supplementary information) [3]. Fig. 1a represents an AFM image of Gd nanoparticles used in the growth of the SWCNTs. Fig. 1b displays the area within the dashed region in Fig. 1a at a higher magnification. The AFM results indicate that the diblock copolymer templating method is suitable to obtain large uniform deposition of the nanoparticles with an average diameter of 1.9 nm and a narrow size distribution (less than 10%). Eu nanoparticles, prepared using the same method, showed similar results. Fig. 2a and b show a representative bright-field transmission electron microscope (TEM) image of Eu- and Gd-catalyzed SWCNT (hereafter referred as Eu-SWCNT and Gd-SWCNT) bundles respectively. Further investigation by high resolution TEM (HRTEM) images show Gd-SWCNTs (Fig. 3a) and Eu-SWCNTs (Fig. 3b) with an average diameter of ~2.05 nm.

In addition to TEM, the growth of SWCNTs was further confirmed by Raman spectroscopy (Fig. 4). Raman spectroscopy is an important characterization tool for carbon nanotubes because it provides information on the diameters, purity, and electronic properties of SWCNTs [7]. The Raman spectrum for the Gd-SWCNTs (Fig. 4a) shows a G band at 1591 cm$^{-1}$ with a down-shifted G$'$ band at 1549 cm$^{-1}$ [7]. The additional Raman peaks such as D, iTOLA, and G$'$ present in Fig. 4a are due to double resonance. These spectral features occur by elastic scattering due to defects on the nanotubes or inelastic scattering by phonon emission [7]. The D band (Fig. 4a) at 1318 cm$^{-1}$ represents a disorder-induced mode in graphite [7]. It usually occurs when there are defects in the carbon and thus considered a measure of sample purity [7]. The D/G band ratio for Gd-SWCNTs is about 0.11, indicating only a small amount of SWCNTs have defects. The G$'$ band at 2610 cm$^{-1}$ occurs at approximately twice the wavenumber as the D band and is known as the overtone mode of D band. Unlike the D band, the G$'$ mode is not known to occur due to SWCNT defects [7]. The iTOLA band at 1915 cm$^{-1}$ is an effect enhanced by double resonance not found in graphite and is due to the combination of the in-plane transverse optical branch (iTO) and the second phonon from the longitudinal acoustic branch (LA), therefore called a combination phonon mode [7]. Although this band exhibits high experimental dispersion, the occurrence of the double resonance process further corroborates the existence of SWCNTs [7].

Fig. 4b displays Raman spectrum of the Eu-SWCNTs. The Eu-SWCNTs have a G band at 1586 cm$^{-1}$ and a G$'$ band at 1559 cm$^{-1}$, both having a Lorentzian lineshape. The double resonance D, iTOLA, and G$'$ bands for the Eu-SWCNTs are
slightly down-shifted compared to the Gd-SWCNTs and occur at 1309, 1910, and 2610 cm$^{-1}$, respectively. The D/G ratio for Eu-SWCNTs is 0.04 again indicating nearly defect free SWCNTs.

Fig. 4c and d show representative radial breathing modes (RBMs) of the Gd-SWCNTs and Eu-SWCNTs respectively. The RBMs, found in the 100–350 cm$^{-1}$ region of Raman spectra, are unique to SWCNTs and occur at frequencies specific to nanotube diameters [7]. Thus, the displayed spectra (Fig. 4c and d) and the spectra obtained from other locations were analyzed to estimate the nanotube diameters. Since the SWCNTs form bundles, van der Waals interactions among the tubes affect the linear relationship between the RBM frequencies and the tube diameter. To factor in this effect, we used the relationship $d_t (\text{nm}) = \left[238 \text{ cm}^{-1} \text{ nm/}v_{\text{RBM}}\right]^{1/0.93}$, where $d_t$ is the diameter of the tube and $v_{\text{RBM}}$ is a given wavenumber [8]. Our calculations show nanotube diameters for the Gd-SWCNTs range from 0.8 to 2.3 nm, while the Eu-SWCNTs range from 0.8 to 1.5 nm. Although the RBM peaks give a good estimation to the diameters of the SWCNTs, peaks that correspond to diameters above 2 nm have weak intensity and may not be observed in the spectra [7]. This may explain the lack of RBM peaks at diameters above 2 nm for the Eu-SWCNTs even though HRTEM images confirm the presence of these SWCNTs.

There is now a growing body of work that demonstrates growth of SWCNTs from metals other than the conventional Fe, Co and Ni [4,6,9]. Even though a number of mechanisms have been postulated to explain SWCNT growth from these metals, the exact growth mechanism is still unclear. Thus, intensive theoretical studies are currently underway in our laboratory to elucidate the mechanisms of Gd-SWCNT and Eu-SWCNT growth as well as to systematically investigate the efficacy of lanthanoid series elements (La–Lu) to catalyze SWCNT growth.

The successful demonstration of SWCNT growth from Gd and Eu opens avenues for their physio-chemical characterization with potential applications in biomedical imaging and sensing [10–12]. For instance, the toxic Gd and Eu ions possess interesting magnetic and photoluminescent properties, respectively [10,11] and have been widely used in the development of contrast agents for optical [11], MR [10], and CEST imaging [12]. The growth of SWCNTs over Gd and Eu should (a) protect the metals from release in vitro and in vivo, sequestering the metal’s toxicity, (b) amplify the contrast enhancement properties of the metal ion, and (c) allow the conjugation of a variety of biological moieties for targeted molecular imaging/drug delivery.

In conclusion, we demonstrate the successful growth of SWCNTs by inner transition metals, Gd and Eu, using chemical vapor deposition. The Gd and Eu nanoparticles used for growth of SWCNTs were prepared by diblock copolymer templating and had an average size of 1.9 nm with a standard deviation of less than 10%. High resolution transmission electron microscopy and Raman spectroscopy confirm the presence of highly pure Gd- and Eu-SWCNTs with an average diameter of 2.05 nm.

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Appendix A. Supplementary data


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