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Preloading catalysts in the reactor for repeated growth of horizontally aligned carbon nanotube arrays

Huanhuan Xie [a, b], Rufan Zhang [b], Yingying Zhang [a, *], Zhe Yin [a], Muqiang Jian [a], Fei Wei [b, **]

[a] Department of Chemistry and Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China
[b] Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

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ABSTRACT

This work presents a highly efficient and reliable strategy to grow horizontally aligned carbon nanotube (CNT) arrays on surfaces via preliminarily loading catalysts into the reactor. With the heat treatment before the growth of CNTs, the catalysts would migrate from the inner surface of the reactor to the surface of the targeted substrate to induce the growth of aligned CNTs. With this "in-situ catalyst loading" approach, aligned CNTs could be grown on different bare substrates, such as silicon, quartz and sapphire. The growth of CNTs could be repeated up to 50 times with reliable results via only one-time catalyst preloading process, avoiding the deposition of catalysts before each round of growth and the related randomicity, and thus benefiting the mass production of aligned CNT arrays on surfaces.

1. Introduction

Carbon nanotubes (CNTs) have captured tremendous attention due to their excellent properties [1–4] and various promising applications [5–9]. Particularly, CNT arrays grown on surfaces by chemical vapor deposition (CVD), with their macroscale length, low defects and parallel alignment, are ideal candidates for applications in next-generation electronics [10,11], attracting persistent research interests [12–14]. Although significant advances have been achieved toward the controlled synthesis of aligned CNTs on surfaces during the past decade, breakthroughs, especially in aspect of chirality-selected growth and mass production, are still needed to be made for their ultimate practical applications in electronics.

The sizes and the distribution of catalyst nanoparticles (NPs) play important roles in the growth of aligned CNTs on surfaces [15,16]. In a typical process, the catalyst precursors are pre-deposited on the substrate surface. Various deposition approaches, such as drop drying [17], spin coating [18], microcontact printing [19,20], sputtering and electron beam evaporation [21,22], have been employed. The pre-deposited catalyst precursors are reduced through heat treatment in hydrogen during the CVD process, forming catalyst NPs and leading to the nucleation of CNTs. The repeatability of the above "non-in-situ catalyst loading" process is not good due to the randomicity of each loading process and the coarsening/merging of the NPs during the heat treatment. Recently, ultra-high dense CNT arrays on surfaces were prepared with Trojan catalysts, which embedded in the substrate with a pretreatment process and released from the substrate to catalyze the growth of CNTs [23]. Herein, we also developed a catalyst preloading process for the highly efficient growth of horizontally aligned CNTs on surfaces. Different from the Trojan catalyst idea, in our strategy, the catalysts are preloaded into the reactor, then gradually released and transferred to the substrates for the growth of CNTs. Our strategy enables the efficient, reliable and repeated growth of horizontally aligned CNTs on various surfaces.

2. Experimental section

Fig. 1 illustrates our process for the growth of aligned CNT arrays on the bare substrates via preloading catalysts into the reaction chamber, which includes two steps. In this experiment, the reactor is a quartz tube fixed in a tube furnace. In **Step I**, catalyst precursor ($FeCl_3 \cdot 6H_2O$) powder was put in the quartz tube followed by heat treatment in continuous Ar/H_2 gas flow. The catalysts were then ambushed in the quartz tube through the sublimation of

* Corresponding author.
** Corresponding author.
E-mail address: yingyingzhang@tsinghua.edu.cn (Y. Zhang).

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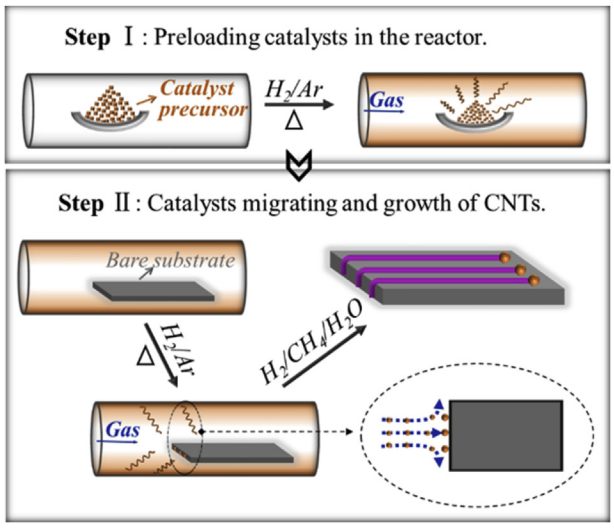

Fig. 1. Schematic illustration showing the preloading of catalyst in the reactor (Step I) and the subsequent repeatable growth of aligned CNTs on bare substrates (Step II). (A color version of this figure can be viewed online.)

$FeCl_3 \cdot 6H_2O$, the reduction of $FeCl_3$ by H_2, and the deposition of Fe. **Step II** involves the migration of the catalysts and the growth of CNTs. When a bare substrate was put into the quartz tube with preloaded catalysts, the catalysts could migrate to the targeted substrate surface during the heating process and lead to the growth of aligned CNT arrays. Noted that **Step II** could be repeated for many times, avoiding the loading of catalysts before each CVD process.

2.1. Preparation of the reactor with preloaded catalysts

A quartz tube (inner diameter: 31 mm) was used for the growth of aligned CNTs. Firstly, a clean quartz tube was annealed in the air at 1000 °C for 8 h. Then, 0.7 g $FeCl_3 \cdot 6H_2O$ powder was put into the quartz tube. The quartz tube was heated from room temperature to 900 °C within 30 min in a continuous gas flow of Ar/H_2 for the deposition of Fe on the inner surface of the quartz tube. Finally, the furnace was cooled down.

2.2. Synthesis of horizontally aligned CNTs with preloaded catalysts in the reactor

Horizontally aligned CNTs were synthesized through CVD. Various substrates, including silicon substrates with 800 nm oxide layer (SiO_2/Si substrate), ST-cut quartz and sapphire, were used to grow horizontally aligned CNTs on surfaces. These substrates were cleaned by ultrasonication in diluted hydrochloric acid, ethanol and deionized water, sequentially. The substrates supported with a quartz boat were put into the center of the quartz tube with ambushed catalysts. The temperature of the furnace was increased to 900 °C in H_2/Ar flow, and remained at 900 °C for 30 min, allowing the migration and the reduction of the catalysts. The growth of CNTs was carried out in H_2/CH_4 with a trace of water vapor at 1005 °C for 20 min. The reaction was terminated by turning off CH_4. Finally, the furnace was cooled down to room temperature in continuous flow of Ar/H_2.

2.3. Characterizations

Scanning electron microscopy (SEM, JEM 7401F) was used to

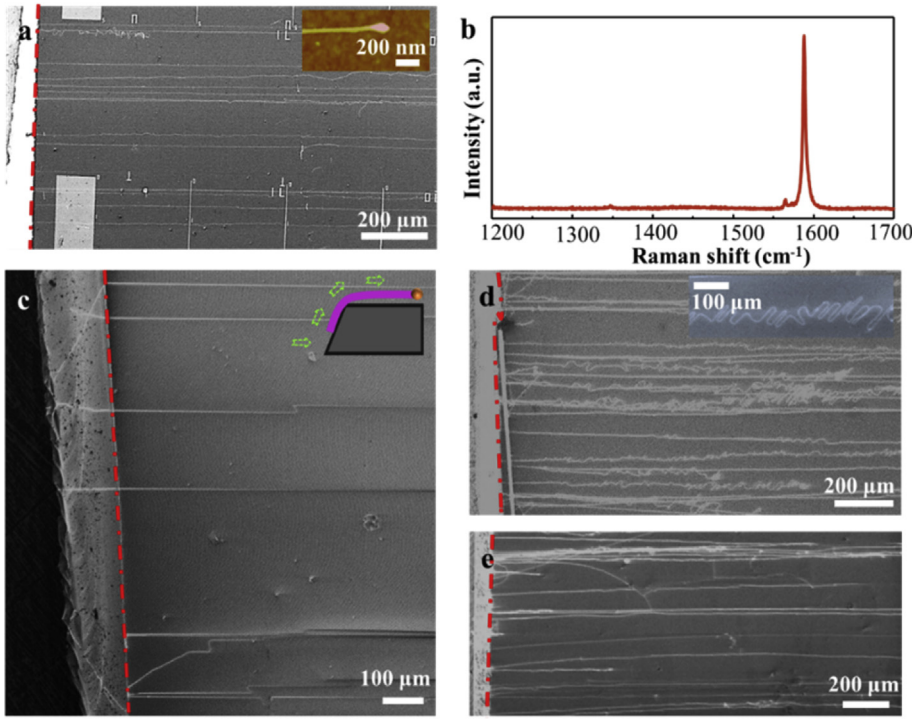

Fig. 2. Characterizations of the as-prepared horizontally aligned CNTs on substrates with preloading catalyst strategy. (a) SEM image of aligned CNT arrays grown on the SiO_2/Si substrate. The markers and trenches along longitudinal direction in Figure a were patterned by photolithography. The inset in Figure a is an AFM image that shows the end of a CNT with a catalyst NP. (b) A Raman spectrum of an as-prepared CNT. (c) The SEM image of the upstream part of the substrate with a slope front surface after the growth of aligned CNT arrays. The inset shows the corresponding illustration of the growth of CNTs. (d) SEM image of aligned CNT arrays grown on the quartz substrate. Inset in Figure d shows the zoomed-in SEM image of serpentine CNTs on the quartz substrate. (e) SEM image of aligned CNT arrays grown on the sapphire substrate. The direction of the gas flow for the growth of CNTs is from the left to right. The red dash line shows the edge of the substrate in the upstream. (A color version of this figure can be viewed online.)