

# PATTERNING OF THREE-DIMENSIONAL CARBON NANOTUBE ARCHITECTURES BY A COMPOSITION TRANSFER APPROACH

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## Introduction

Creating three-dimensional patterned nanoarchitectures on the surface of a substrate is an essential step towards the investigations on their novel properties and the developments of nanomaterials and nanodevices at different length scales. Patterned nano-architectures composed of one-dimensional (1D) nanowires/nanotubes on two-dimensional substrates always exhibit tailored mechanical, thermal, catalytic or optical properties. Among various 1D nanomaterials, carbon nanotube (CNT) is one of most attractive building blocks because of their unique properties originating from the small size, cylindrical structure, and high aspect ratio. If CNTs can be controllably patterned into 3D nanoarchitectures, they will hold promise for a variety of applications in intelligent nanocomposites with hydrophobic surfaces, field emission display, energy conversion and storage, sensor, and catalysis.

The construction of patterned CNT architectures generally relies on the fabrication of patterned catalyst layers or substrates through complicated procedures. Shadow mask, block copolymer micellar films, soft-lithography, and photolithography, were used to pattern iron catalysts for the self oriented growth of CNT architectures [1]. Recently, numerous works on CNT growth with multi-composition catalysts were reported [2], and it was noticed that the growth of CNTs were sensitive to the catalyst composition.

Herein, we proposed the gas-phase transfer process of a second phase metallic composition to modulate the activities and controllably construct the CNT architectures. The appearance of small amount additives may great change the activities of catalyst for CNT growth by over an order of magnitude. As shown in Fig.1. During the annealing process, the compositions on the covering mask were sublimated onto the Fe catalyst layer, which tuned the catalytic activities for

the growth of CNTs. Rilievo- and intaglio-structured CNT architectures can therefore been constructed with the assistance of promoters or inhibitors.

## Experimental

The patterning growth of 3D CNT architectures by a composition transfer process involved several procedures. A SiO<sub>2</sub>/Si (600-nm-thick thermally grown SiO<sub>2</sub> layer) wafer was selected as the substrate. Al<sub>2</sub>O<sub>3</sub> (10.0 nm), Fe (1.0 nm) and MgO (1.0 nm) were sequentially deposited on the substrate as the catalyst film by the electron beam evaporation. The commercial mesh grids with different composition for transmission electron microscope (TEM) analysis, such as Mo, Au, Cu, Fe, Ni grids, were selected as the masks. Firstly, the TEM grids of various patterned structures were laid onto the surface of MgO/Fe/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/Si substrate. They were then set into a horizontal tubular furnace for the CVD growth of CNTs through the pyrolysis of ethylene. Generally, the temperature of the furnace rised to 750 °C under Ar atmosphere, and H<sub>2</sub> was then introduced to anneal the catalyst film for 10 min before the introduction of ethylene to start the growth of CNTs. After the CVD growth of patterned CNTs, the furnace was cooled down to room temperature under Ar protection. The typical flow rates for Ar, H<sub>2</sub>, and ethylene were 250, 200, and 100 sccm, respectively. The as-obtained products were characterized using scanning electron microscopy (SEM, JSM 7401F), TEM (JEM 2010), Raman spectrophotometer (Renishaw RM2000 with laser excitation line at 633.0 nm), X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM), and contact angle meter (Dataphysics OCA20 with 2 μL pure water drops).

## Results and Discussion

To demonstrate the above mentioned concept, rectangular patterned Mo/Au grids were selected as the promoter/inhibitor to illustrate the soft composition transfer strategy. Fig. 2a-b show the related self-organized 3D CNT architectures. With the masking of Mo grids as the promoters, patterned CNT architecture was obtained, indicating the Mo grid tuned the growth behaviors of CNTs obviously. Without the cover of Mo grids, the Fe catalyst gave rise to short CNT films. When covered with grid lines of Mo grids, the aligned CNTs were relatively high, and they split outwards. Under the cover with the crosses of Mo grids, some long aligned CNT arrays stood as CNT pillars. Fig. 2b shows the patterned CNT films with the cover of Au grids as inhibitors. The pattern of Au grid was printed onto the CNT films that CNTs can hardly grow under the cover of Au grid while dense and short CNT arrays can be synthesized without the coverage. With detailed SEM characterization, CNTs were found to retain their alignments during the mask-assisted self-organization process (Fig. 2c). To compare the qualities of CNTs in covered and uncovered area, Raman spectra of CNTs in different areas were presented in Fig. 2d. Raman spectra

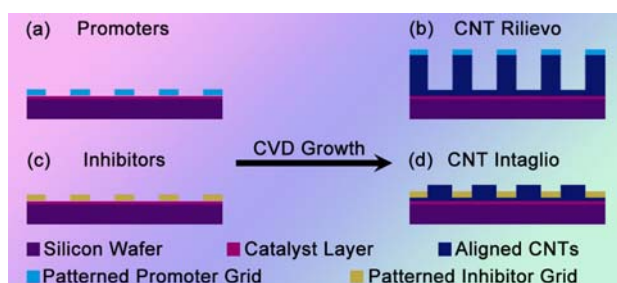
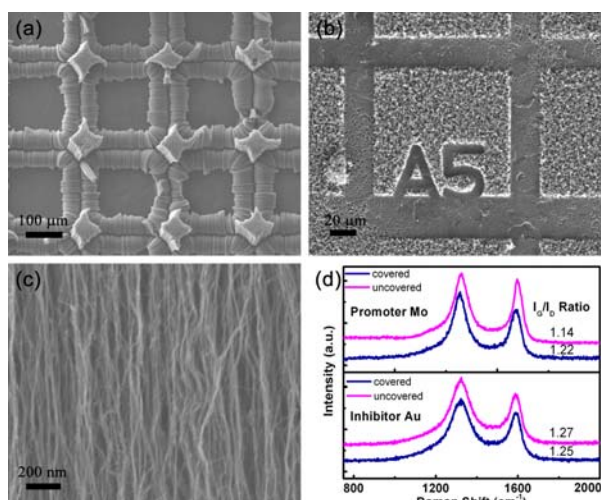


Fig. 1 The schematic illustration of the gas-phase transfer process for the construction of 3D CNT architectures.

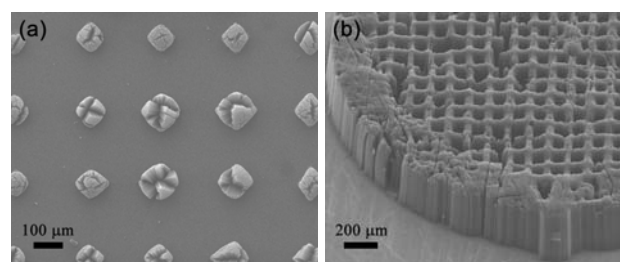


**Fig. 2** (a) A promoter (Mo grid) patterned growth of rilievo-structured CNT architectures; (b) An inhibitor (Au grid) patterned growth of intaglio-structured CNT architectures; (c) the SEM micrograph of the aligned CNTs in promoter patterned growth; (d) Raman spectra CNT arrays obtained in the Mo and Au grid assisted CVD process

with and without the cover of patterned grids showed similar band shapes.

The Mo grid masked growth was further selected as the model to investigate the mechanism of patterned growth. XPS spectra were employed to decide whether Mo, the second active phase, was transferred onto the Fe catalyst layer. After the annealing process, the XPS spectrum of Mo covered area showed an obvious Mo 3d peak, while no Mo signal can be detected on the area without the cover of Mo grids. The addition of small amount of Mo into Fe catalysts can stabilize the catalyst particles and form new phases that were more active in the synthesis of CNTs [3].

Based on the understanding of this process, a family of CNT nanoarchitectures can be designed. Using Mo as a growth switch, walnut-like CNT architectures (Fig. 3a) were obtained on solely inactive thin Fe catalyst layer (0.5 nm), with 3 min annealing and 10 min growth. In this pattern, CNT protuberance formed in the places corresponded to the cross areas in the Mo grid. It was supposed that the sublimation of Mo in these areas realized the growth of these periodic CNT patterns, while inadequate Mo sublimation fail to support the growth of CNT architectures. With prolonged annealing duration (10 min), CNT monolith can be fabricated as shown in Fig. 3b. Long annealing duration ensured the migration of adequate Mo onto the catalyst films covered by both grid lines and crosses, so that grid-patterned monolith constructed by CNT arrays can be fabricated. After the peeling off of this CNT monolith, only thin CNT films were found in the holes without the cover of Mo grid. The growth rate of aligned CNTs covered by the mask was estimated to be two orders of magnitude higher than that without the cover. Combined the outstanding properties of pristine CNTs and the hierarchical structures, the CNT architectures obtained by the composition



**Fig. 3** Different CNT architectures obtained with Mo grid as the mask. (a) walnut-like CNT architectures with 3-min annealing; (b) CNT monolith obtained with 10-min annealing.

transfer process were demonstrated to be of attractive properties. In this process, the hierarchical CNT monolith showed outstanding hydrophobic property with a contact angle

of  $152^\circ$  (pristine substrate of  $81^\circ$  and uniform CNT film of  $140^\circ$ ). Moreover, the CNT monolith exhibited the advantages of multi-stage structure, high surface area and high thermal conductivity, and was promising as new nanomaterials for micro reactor serving under extreme conditions [4]. Finally, the templates for this method can be easily obtained through micromachining, indicating the feasibility of this process in the scaling up and industrial application.

## Conclusions

In summary, a novel approach to construct various 3D patterned CNT nanoarchitectures through composition transfer method was reported. Utilizing masks such as Mo, Au, Cu, W, and Ni micro grids, the promoter/inhibitor phase can be patterned onto the catalyst layer and rilievo- or intaglio-structured CNT nano-architectures formed. The synergetic effect of chemical doping and gravity induced assembling were speculated to be responsible for the complex self-organization. The as-obtained CNT nanoarchitectures showed super-hydrophobic properties. A facile alternative approach for constructing a family of functional CNT architectures were demonstrated, which will benefit the exploration of the nanoscale science and technology.

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