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Fabrication of patterned carbon nanotubes with adjustable arrays through controlled mesoscopic dewetting

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ABSTRACT

Here, we report the synthesis of aligned carbon nanotube (CNT) bundles with adjustable arrays by a non-lithographic and low-cost strategy. A polystyrene/ferrocene patterns on silicon (Si) substrate was prepared through controlled mesoscopic dewetting of dilute polystyrene/ferrocene solution. A variety of regular patterns, including ladder, stripe and scale, were synthesized simply by changing the solution concentration. Ultraviolet (UV) irradiation effectively cross-linked polymer skeleton and made it suitable for structure-directing agent. In the sequent pyrolysis, polystyrene skeleton was decomposed and ferrocene was converted into the skeleton of inorganic patterns simultaneously. Aligned CNT bundles guided by the catalytically functionalized inorganic patterns were initiated to grow. This methodology opens up a new avenue for fabricating CNT arrays in a simple and controllable manner.

1. Introduction

Due to their extraordinary physical properties, carbon nanotubes (CNTs) are considered to be a potential material for next-generation micro- and nanoelectronics [1–4]. But to take full advantage of their properties, it is highly desirable to have aligned CNTs with regular micropatterns so that they can be effectively incorporated into devices [5]. The micropatterned CNT architectures have been achieved by chemical vapor deposition (CVD) on predesigned catalyst patterns or substrate patterns, obtained by a variety of strategies including offset printing, standard lithography, and soft lithography [6–9]. By means of the available techniques, the space resolution for the preparation of CNT patterns on substrate has been down to micrometer scale. However, the time and cost of the mentioned technologies are the major barriers limiting their practical application. A non-lithographic, simple and low-cost technique is more desirable.

Dewetting process of a dilute monolayer should be especially interesting because it allows for a higher degree of convection-induced motion during evaporation. The nonvolatile solutes (e.g., polymers, proteins, viruses, bacteria, DNA, microspheres, nanocrystals, carbon nanotubes, etc.) contained within a sessile droplet (i.e., unconstrained liquid) readily assemble into a diverse range of intriguing one- or two-dimensional structures, possessing dimensions of a few hundred submicrons and beyond [10–12]. It's becoming an area of significant topical interest and has particular potential in the context of self-organized microstructures. A number of groups have exploited the fingering instabilities in drying nanofluids to form linear assemblies of particles exhibiting an impressive degree of pseudo-one-dimensional order. One-step self-assembly, alignment, and patterning of organic semiconductor nanowires and spontaneous formation of nanoparticle stripe patterns have been achieved through controlled evaporation of confined microfluids [13–15]. Particularly, a methodology preparing mesoscale polymer patterns simply by casting a dilute polymer solution on solid substrate solution though a small gap has attracted more and more attention [16]. Dissipative structures are formed in the evaporation of polymer solution and sequent dewetting of the polymer film on the substrate cooperatively induce regular pattern formation. Recently, we synthesized patterned CNTs with adjustable array utilizing honeycomb-structured amphiphilic block polymer/inorganic precursor hybrid films [17]. It was found that cross-linked polymer matrix could act as structure directing agent to form catalytically functionalized inorganic templates and guide the growth of CNTs. Here, we present a novel methodology to prepare functionalized inorganic patterns *via* controlled mesoscopic dewetting and sequent pyrolysis. The aligned CNT bundles growing from the inorganic patterns would be potential candidates for engineering applications.

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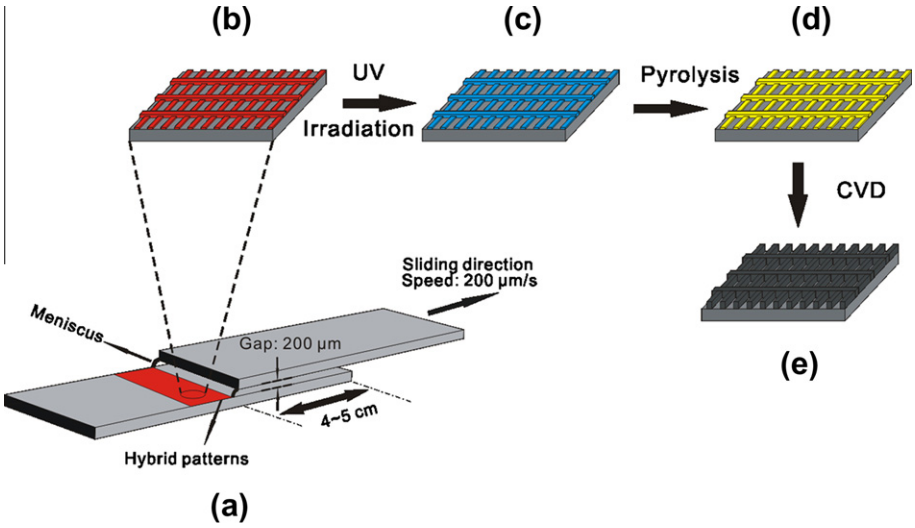

Fig. 1. Schematic pictures of fabrication process of aligned CNT arrays with micropatterns on substrate. (a) The schematic illustration of the experimental set-up for the hybrid micropatterns preparation. (b) Highly regular polystyrene/ferrocene hybrid pattern was formed on substrate after total evaporation of solvent. (c) Polymer matrix was cross-linked and the pattern was preserved after photochemical process. (d) Ferrous inorganic pattern was formed on substrate after pyrolysis. (e) The pattern with the walls of aligned CNT bundles was formed under guidance by the inorganic pattern.

The fabrication process is schematically shown in Fig. 1. A mixture of polystyrene/ferrocene (5/1, w/w) was dissolved in dichloromethane (CH_2Cl_2). Then the solution was introduced into the gap between two Si plates, and the upper Si plate was allowed to slide over the lower with a constant velocity (Fig. 1a). A thin and continuous liquid film of polymer solution followed the edge of the top Si plate and polymer hybrid patterns were formed on the bottom plate after solvent evaporation (Fig. 1b). Deep UV irradiation resulted in cross-linked polymer skeleton with preserved patterns and improved thermal stability (Fig. 1c). Such a cross-linked polymer skeleton could act as structure-directing agent in the sequent pyrolysis, and eventually was replaced by the oxides of ferrocene (Fig. 1d). In the sequent CVD process, aligned CNT bundles were initiated to grow guided by the catalytically functionalized inorganic patterns (Fig. 1e).

2. Experimental

2.1. Reagents and materials

Polystyrene (weight–average molecular weight, M_w = 2,000,000; M_w/M_n = 1.30) were obtained from Alfa Aesar, China. Ferrocene and CH_2Cl_2 were purchased from Shanghai Chemical Reagent Plant. All the chemical reagents were used without further purification.

2.2. Preparation of hybrid micropatterns

To control the pattern-formation process, we fabricate an apparatus composed of two moving substrate holders. A Si plate (70 mm × 20 mm) was attached to a substrate holder, which moved smoothly at a speed set by a computer-controlled driving system. Another Si plate was set on the other substrate holder. The Si plates overlapped by about 4–5 cm and were separated by a narrow gap of 200 μm. The schematic illustration of the experimental set-up is shown in Fig. 1a. Polystyrene and ferrocene were mixed with a fixed weight ratio (5/1, w/w) and dissolved in CH_2Cl_2. The CH_2Cl_2 solution concentrations range from 2 g L^{-1} to 6.3 g L^{-1}. 200 μl of solution were added to the gap between the two Si plates, and the upper glass plate was moved linearly at a speed of 200 μm s^{-1}. After complete solvent evaporation, regular hybrid micropatterns were formed on the stationary bottom Si plate.

2.3. Preparation of micropatterned ferric oxide templates

The hybrid micropatterns were photo-chemically cross-linked at 30 °C in a UVO cleaner (ZWLH-5, Tianjin, China) at the presence of air, by exposing the pattern into UV light. The cleaner generated UV emission at a wavelength of 254 nm and power of 500 W. The distance between the UV source and the pattern surface was 10 cm. After 4 h UV exposure, the cross-linked patterns were heated to 450 °C within 2 h and held for another 5 h under air atmosphere. During the pyrolysis, ferrocene turned into oxide and replaced the polymer skeleton eventually.

2.4. Preparation of CNT arrays

Aligned CNT arrays were synthesized by thermal chemical vapor deposition (CVD) in a 40 mm diameter quartz tube furnace. The tube furnace was preheated to 750 °C and then the templates were inserted into the chamber. An Ar/H_2 gas mixture was used as the buffer gas and pure acetylene served as the carbon source. In the growth process, a constant flow rate of 500/200/78 sccm for $Ar/H_2/C_2H_2$ was used. The growing time was 10 min.

2.5. Characterization and apparatus

Hybrid patterns were observed by optical microscopy (MODEL ECLIPSE ME600, Nikon, Japan) and scanning electrical microscopy (S4800, Hitachi, Japan). EDX was performed on a JXA-8100 Electron Probe Micro-Analysis, equipped with an EDX unit by Oxford Instruments. The morphology and structure of patterned CNTs were also characterized by Hitachi S4800 scanning electron microscope (SEM). A 10 keV electron beam was used for the observation with a working distance of 8 mm in order to obtain secondary electron images. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a PHI Quantum 2000 spectrometer using monochromated X-rays from an Al Kα source with a takeoff angle of 45° from the surface plane. The morphology and structure of the CNTs were characterized by high-resolution transmission electron microscopy (TECNAI F-30) with an acceleration voltage of 300 kV. The TEM specimens were prepared by dispersing the CNTs in ethanol. A drop of the suspension was deposited on a carbon-film-coated copper grid.