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.

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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, nano-crystals, 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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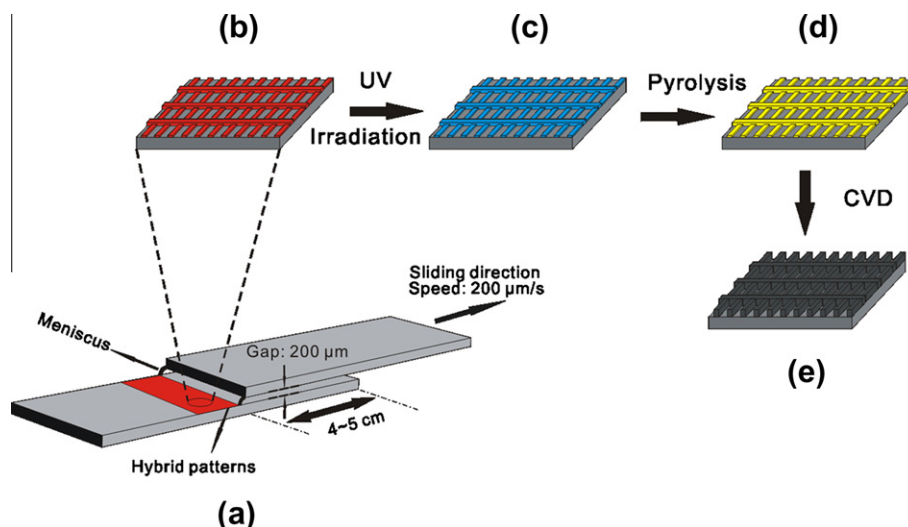
Fig. 1. Schematic pictures of fabrication process of aligned CNT arrays with micropatterns on substrate. (a) The schematic illustration of the experimental set-up for the hybrid micropatterns preparation. (b) Highly regular polystyrene/ferrocene hybrid pattern was formed on substrate after total evaporation 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$_2$H$_2$ 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.

3. Results and discussion

The key point of the formation of highly regular polymer patterns on substrate is that a narrow, thin and liquid film of polymer solution with a receding meniscus is continuously supplied from a small gap between two plates. In order to achieve that, two Si plates were overlapped and separated by narrow spacers and a computer-controlled driving system was employed to obtain constant sliding velocity. Upon polystyrene/ferrocene solution with a concentration of 3.3 g L^{-1} was charged into the gap between two Si plates, the upper plate was pulled linearly with a fixed velocity of 200 μm s^{-1}. A thin liquid film and meniscus was continuously formed, observed by naked eyes. After complete solvent evaporation, the obtained film exhibits beautiful nacre color (Fig. 2a), as the expected sunlight diffraction and interference effects from the ordered structures on substrate. Optical microscopy observa-

tion reveals that uniform ladder-like patterns were formed, as shown in Fig. 2b. An FFT of the scanning electronic microscopy (SEM) image was shown in the inset, where two sets of orthogonal Bragg peaks of the stringers (sliding direction) and rings (normal to sliding direction) were found. The formation of ladder-like polymer patterns on substrate by the similar methodology was found and explained by Yabu and Shimomura, which was attributed to the simultaneous occurrence of stick–slip motion and fingering instability [16]. It should be noticed that the incorporated ferrocene has no influence of the dewetting process and pattern formation, which is essential for the growth of aligned CNTs arrays.

However, the obtained polystyrene/ferrocene patterns cannot initiate the growth of CNT. Upon heating up to 100 °C (the glass transition temperature, T_g, of the polystyrene), the as-prepared patterns began to melt then collapsed and totally disappeared at 130 °C. The poor thermal stability of polystyrene inevitably causes
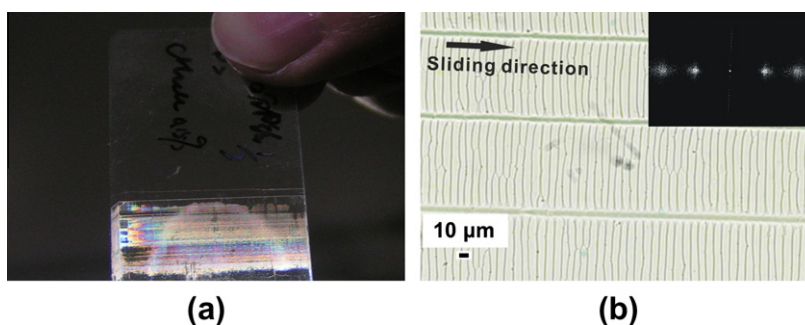
Fig. 2. (a) The ladder-like hybrid pattern prepared from polystyrene/ferrocene solution with the concentration of 3.3 g L^{-1}. (b) Optical microscopy image of ladder-like polystyrene/ferrocene hybrid pattern, the inset shows its laser diffraction pattern.
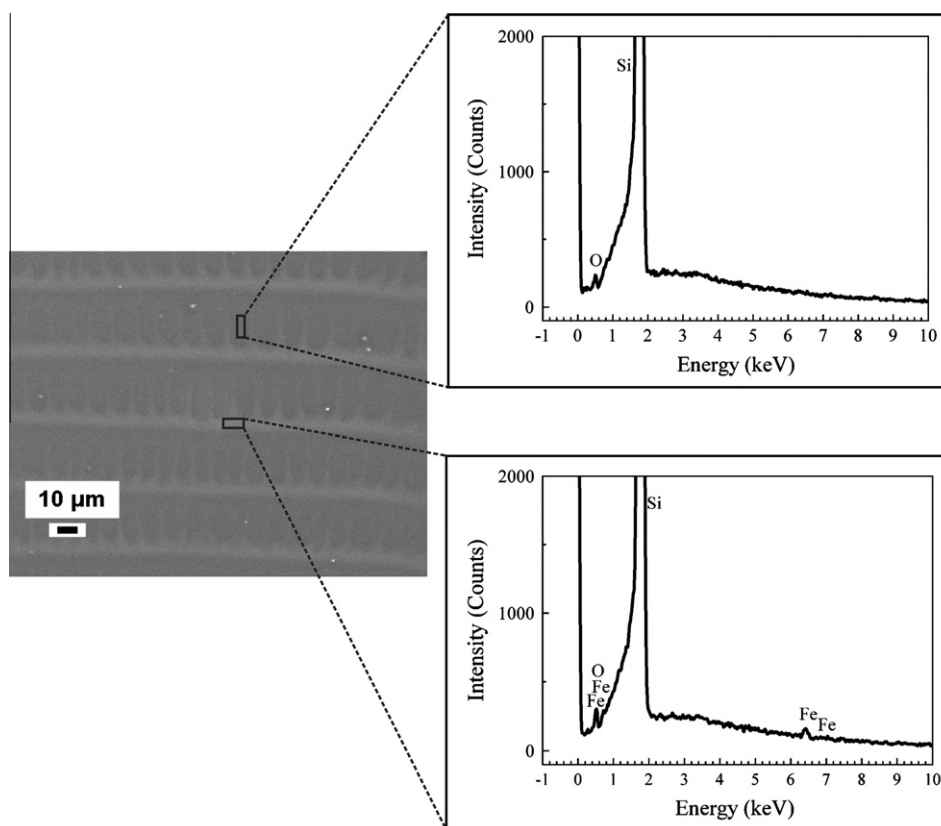
Fig. 3. BSE image of cross-linked ladder-like hybrid patterns pyrolyzed at 450 °C for 5 h and the corresponding EDX spectroscopy in the selected areas.

the structure-directing action of the polymer skeleton invalid in the following CVD process. It is assumed that the ferrocene particles sink into the polymer melt and are isolated from H_2 (reducing agent) and acetylene gas (carbon source). Crosslinkage should be an efficient method targeting the stable film structure against solvents and heat annealing [18]. Under deep UV irradiation, α-H atoms on polystyrene main chains are abstracted, then macroradicals are formed. When two macroradicals are close to each other, the cross-linkage may occur. The cross-linked polystyrene films became resistant to a wide range of organic solvents and thermally stable up to 250 °C, an increase of more than 150 K as compared to the uncross-linked films [19]. In addition, since photochemical cross-linkage is usually completed at room temperature, the operation hardly deforms the patterns, which is necessary for the following template applications. As reported in our previous research, a variety of inorganic patterns templating from robust honeycomb-structured polymer/inorganic precursor hybrid films have been prepared taking advantage of the simple operation [20,21].

After 4 h UV irradiation, the ladder-like patterns were well preserved (see Supplementary Fig. S1). The following pyrolysis process was monitored by X-ray photoelectron spectroscopy (XPS). The atomic fraction of C decreases up to zero, indicative of total decomposition of polystyrene after the pyrolysis. The peak at 710.9 ($Fe2p_{3/2}$) suggest that ferrocene is converted into Fe_2O_3 (see Supplementary Fig. S2). Since back scattering electrons (BSEs) are sensitive to atomic number, BSE microscopy was used to characterize the substrate surface features. As shown in Fig. 3, bright ladder-like pattern are found on Si substrate. The contrast stems from the large difference of BSE emission coefficient between Fe and Si. Furthermore, the Energy-dispersive X-ray (EDX) spectroscopy in the selected areas definitely demonstrate the exclusive existence of Fe in the ladder-like pattern areas, which is consistent with the BSE results. These inorganic patterns have the identical shape with that of the as-prepared patterns, suggesting that ferrocene was oxidized, sunk down and overlapped the ladder-like patterns during the pyrolysis. However, the high temperatures associated with the CVD technique might produce an undesired interaction of the metallic catalyst with the Si substrate, which could deteriorate the catalytic efficiency. It has been reported that the thickness of the native silicon oxide layer play an important role on the growth of CNTs on Si substrate catalyzed by Fe [22].

If the native silicon oxide layer is thinner than 5 nm, it cannot prevent Fe diffuse through silica layers and react with the Si substrate during the CVD process. The formed $FeSi_2$ and $FeSiO_4$ are known for their noncatalytic activity for CNT growth [23]. In our previous research, this chemistry has been utilized to synthesize a pair of matchable serial-port-shaped CNT patterns, i.e., the isolated CNT bundle arrays and the honeycomb-like skeleton with the walls of vertically dense CNT bundles, on Si wafer [17]. Cross-sectional secondary electron image, as shown in Fig. 4a, clearly indicates that the height of the formed inorganic patterns after pyrolysis is close to 50 nm, which is thick enough to prevent the undesirable chemical reactions.

CVD was operated with constant flow rate of 500/200/78 sccm (standard-state cubic centimeter per minute) for $Ar/H_2/C_2H_2$. The growth temperature was 750 °C and the growth time was about 10 min. Templating from the highly ordered inorganic ferrous patterns, aligned CNT arrays with ladder-like patterns were formed after CVD process, as show in Fig. 4b. Side view demonstrates that the aligned CNTs are perpendicular to substrate without collapse (Fig. 4c), thanks to the supporting force among the continuous CNT bundles counteracted the effect of gravity. The well-aligned CNT bundles have a uniform length of 25 µm and can be controlled by changing the time of CVD process. The formed CNTs are multi-walled tubes having an average diameter of 15 nm, as confirmed by high-resolution transmission electron microscopy, as shown in Fig. 4d. The electrical and electrochemical properties of the formed CNT array were also investigated. The measured electrical resistivity is 1.3 Ω cm. The current–voltage (IV) curve (see Supplementary Fig. S3) shows nearly linear relationship between current and voltage, which is good indication of metallic conductivity. Cyclic voltammetry (CV) curve of the CNT electrode (see Supplementary Fig. S4) in 0.5 mM $K_3Fe(CN)_6$ with 0.4 M KNO_3 as a supporting electrolyte indicated that the CNT array shows good electrocatalysis activities.
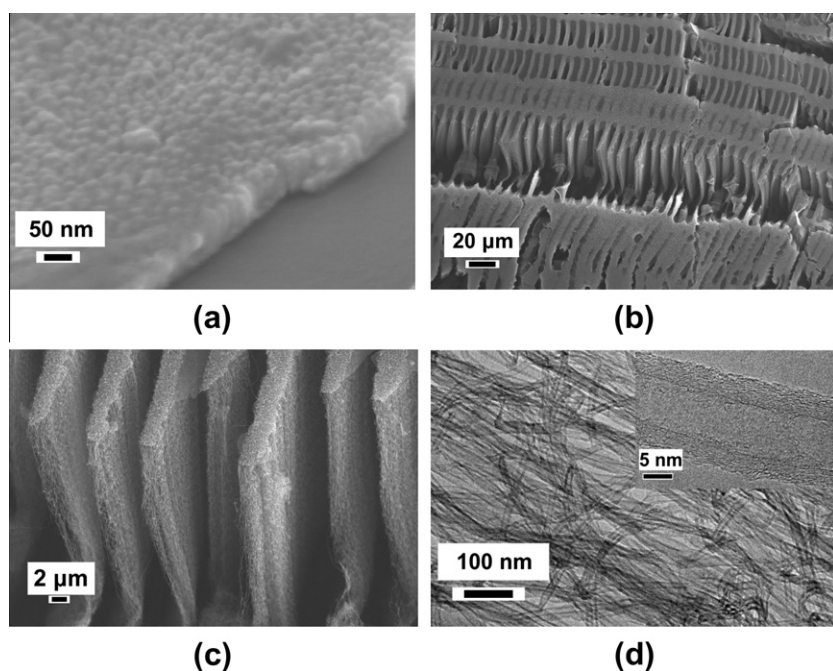
Fig. 4. (a) Cross-section SEM image of cross-linked ladder-like hybrid patterns pyrolyzed at 450 °C for 5 h. SEM images of the aligned CNTs with ladder-like pattern, viewed form (b) top and (c) side, respectively. (d) HRTEM image of the patterned CNTs, the inset showed one multiwalled carbon nanotube.
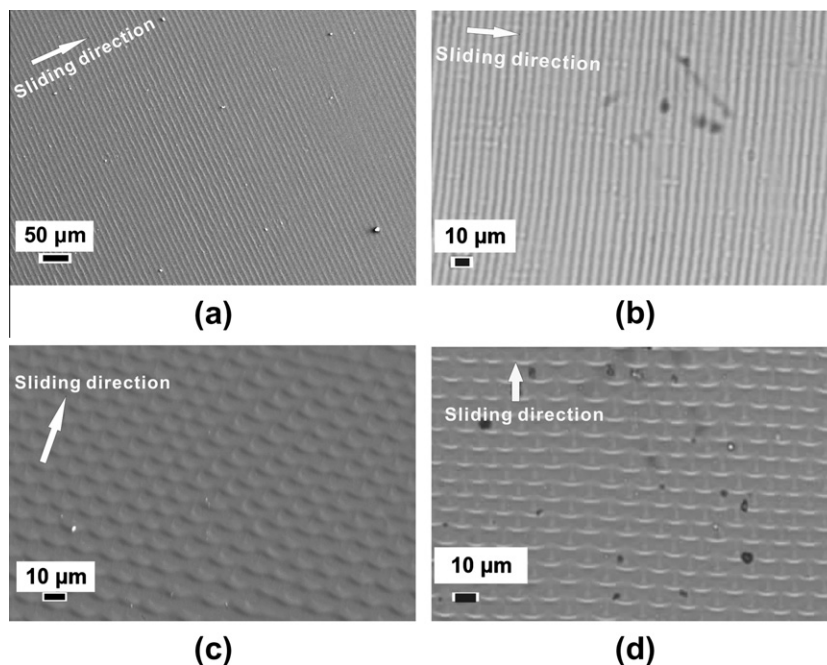
Fig. 5. Scanning electronic and optical microscopy images of patterned hybrid films prepared from polystyrene/ferrocene solution with the concentration of 2.0 g L^{-1} (a and b); 6.0 g L^{-1} (c and d).
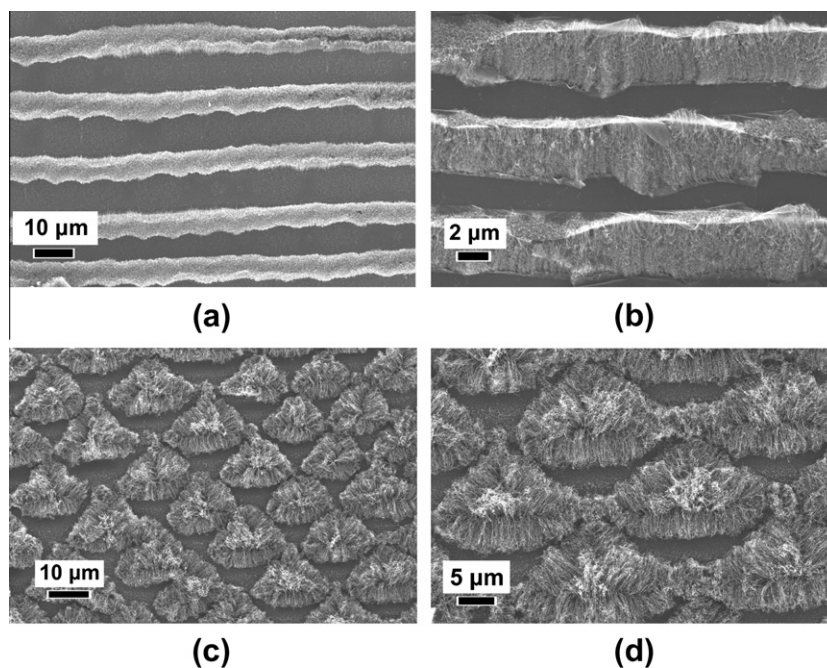
Fig. 6. SEM images of the vertical aligned CNTs with stripe-like pattern, viewed from (a) top and (b) side, respectively. (c) SEM view of the vertical aligned CNTs with scale-like pattern. (d) Higher magnification of (c).

Many other polymer patterns have been created by dissipative structures constructed in the forming of homogeneous liquid film and sequent dewetting of the polymer film on substrate. The shape of obtained polymer patterns are significantly influenced by the concentration of polymer solution [16]. When the solution concentrations are 2.0 and 6.0 g L^{-1}, regular strip- and scale-like patterns, as shown in Fig. 5, respectively, are formed on Si substrate after dewetting. To the best of our knowledge, it is the first time that this kind of scale-like patterns in hexagonal arrangement is reported. The formation mechanism is being investigated. After the same

UV irradiation, pyrolysis and CVD process, strip- and scale-like CNT bundles are formed on Si substrate, as shown in Fig. 6. The fabrication of more complex patterns and their template applications are currently under investigation.

4. conclusions

In summary, we have taken advantage of controlled mesoscopic dewetting process to prepare regular polystyrene/ferrocene patterns on Si substrate. By changing the solution concentration, a

variety of patterns, including ladder-, stripe-and scale-like patterns are formed. By further UV exposure, polystyrene skeleton was cross-linked to act as structure directing agent. In the following pyrolysis, the incorporated ferrocene was converted into Fe_2O_3 and replaced the skeleton of polymer matrix to form the ferrous inorganic patterns with catalytic activity for carbon nanotube growth. Starting from ferrous inorganic patterns prepared, aligned CNT arrays with ladder-like, stripe-like, and scale-like patterns were synthesized after the CVD process. The controlled CNT arrays have potential applications in microelectrics, supercapacitor, field-emission device and other areas. We envision the possibility of developing an even richer family of surface patterns and CNT arrays.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2012.08.017.

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