Journal of Colloid and Interface Science 407 (2013) 556–560

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Short Communication

Small angle X-ray scattering study of carbon nanotube forests densified into long range patterns by controlled solvent evaporation

Ludovic F. Dumée [a,b,*], Kallista Sears [c], Jürg A. Schütz [d], Niall Finn [d], Mikel Duke [b,e], Stephen Mudie [f], Nigel Kirby [f], Stephen Gray [b,e]

[a] Institute for Frontier Materials at Deakin University, Pigdons Road, Waurn Ponds 3216, Victoria, Australia
[b] Institute for Sustainability and Innovation, Victoria University, Hoppers Lane, Werribee 3030, Victoria, Australia
[c] CSIRO Materials Science and Engineering, Private Bag 10, Clayton South 3169, Victoria, Australia
[d] CSIRO Materials Science and Engineering, Waurn Ponds 3216, Victoria, Australia
[e] College of Engineering and Science, Victoria University, Ballarat Road, Footscray Park 3011, Victoria, Australia
[f] Australian Synchrotron, 800 Blackburn Road, Clayton 3169, Victoria, Australia

ARTICLE INFO

Article history:
Received 31 January 2013
Accepted 12 June 2013
Available online 27 June 2013

Keywords:
SAXS alignment analysis
Long range structuring
Emergent properties
Spontaneous order
Carbon nanotubes forest densification
Aligned carbon nanotube patterns

ABSTRACT

Although emergent properties from self-assembly of carbon nanotubes have been described in various forms there is so far no systematic process for the preparation of dense arrays of aligned nanotubes. Here we present a systematic study on the analysis of the alignment of carbon nanotubes within solvent densified carbon nanotube forests. Highly periodic patterns with length scales of the order of the millimetres were generated and characterized by electron and optical micrographs and compared to results from small angle X-ray scattering performed at various incident beam angles. The impact of the different solvents was also discussed in light of the densification process and in relation to solvent properties.

1. Introduction

One of the most important challenges with Carbon Nanotube (CNT) research is related to their integration and controlled orientation within functional composite materials [1]. Issues related to CNT aggregation [2], alignment or self-assembly when dispersed in a solvent or polymer matrix have been attributed to very strong van der Waals forces generated between CNTs by their large specific surface area [3]. This limits the performance of these composites and prevents researchers from fully benefiting from the remarkable CNT properties [4]. Highly ordered orientation of CNTs is particularly sought after in order to direct heat and electrical transfers, support asymmetric mechanical loadings within flexible structures, induce or prevent wetting or create aligned pore arrays across otherwise impermeable membrane matrixes [5–7]. Applications where orientation controlled CNTs are critical include separation where through pores are desired [5], sensing where carbon nanotube tips may play a greater role than side walls [8], nanoelectronic devices with anisotropic electrical conduction [9] or tribology, where surface patterning will govern phenomenon such as dynamic wetting or frictions [10]. In order to facilitate the investigation of CNT properties, dispersions of CNT have been used to form randomly distributed structures, which can be used to study the natural properties of CNT as scaffolds [11–13]. Although the fabrication of high density and aligned CNT structures can be achieved by densifying CNT webs or pristine powder [14], recent research suggested solvent infiltration within CNT macro-bundles as an alternative facile route to these processes [15]. Solvent withdrawal leads adjacent CNTs to densify under the influence of capillary forces, thus enhancing the van der Waals potential and leading to localised high density regions within patterned structures. Previous studies have focused on a single solvent or on pre-patterning the CNT growth [16,17], rather than correlating the relation between solvent properties and capillary-induced densification.

In this work we report for the first time (i) on the impact of the solvent properties on the engineered densification of CNT forests, and (ii) on a novel method to qualitatively characterize the emergent alignment change across large CNTs arrays. The process of solvent densification is represented in Fig. 1. In this process, CNT forests were carefully dipped into pure or mixed solvents in order to avoid the solvent front advancing within the forest too quickly, which would have caused the densification of the aligned arrays of

* Corresponding author at: Institute for Frontier Materials at Deakin University, Pigdons Road, Waurn Ponds 3216, Victoria, Australia.
E-mail address: ludovic.dumee@deakin.edu.au (L.F. Dumée).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.06.018

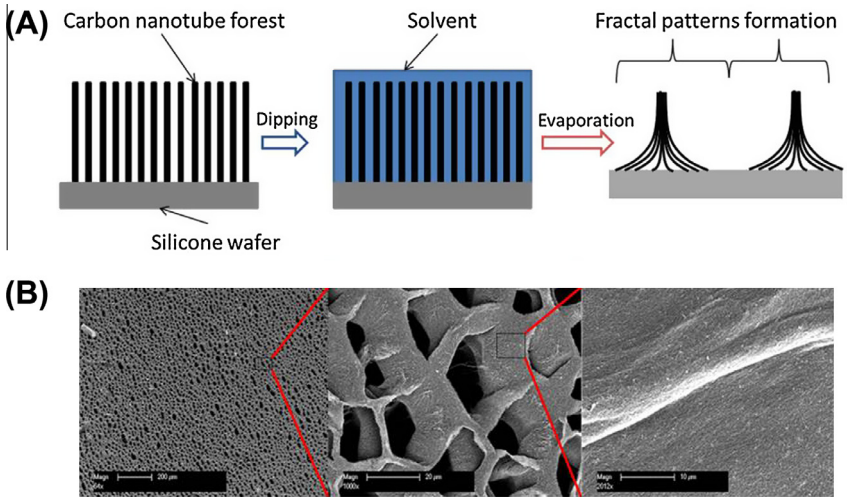

Fig. 1. (A) Process of solvent densification of aligned CNT forest and (B) Scanning Electron Micrographs (SEM) of a typical forest after solvent densification with a tetrahydrofurane (THF)/dimethylformamide (DMF) 10/90 mixture; the high purity multi walled CNTs used had an approximate spacing of 100 nm and were vertically grown as aligned forests. The CNT density on the surface was close to 10^{10} CNT cm^{-2}. The average CNT diameter was 10 nm (±2 nm) with a length of ~300 μm. The CNTs were grown by chemical vapour deposition onto silicon wafers following a protocol described in the supplementary material.

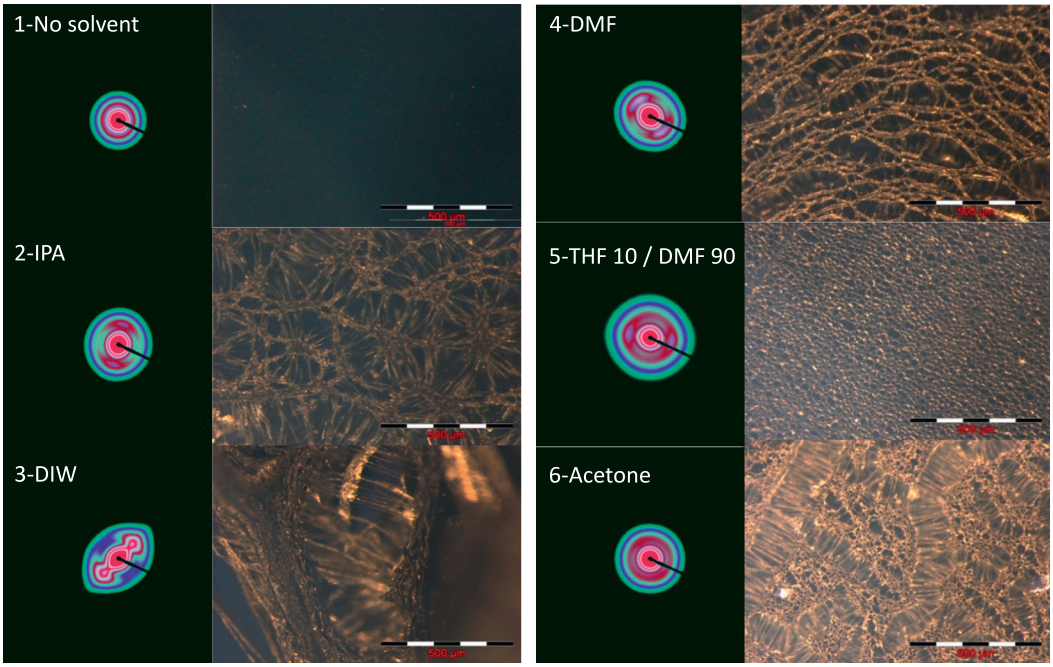

Fig. 2. Confocal micrographs of (1) un-treated CNT forest and after dipping/evaporation in (2) Isopropanol (IPA), (3) Deionised water (DIW), (4) DMF, (5) THF/DMF and (6) acetone; The CNTs were grown by chemical vapour deposition at the CSIRO following a procedure detailed in [24,25]. Corresponding SAXS scattering patterns, acquired at the Australian Synchrotron, are shown on the left hand side of each optical image. The scale bar on each image corresponds to 500 μm. While the CNT forest is highly aligned along the growth axis, it has a large degree of entanglement and tortuosity which is isotropic in the *X*–*Y* plane perpendicular to the incident X-ray beam, which leads to the circular features. For comparison an image of (1) in red temperature colour scheme is shown in the S.I. Fig. 5.

Table 1
Correlation between viscosity, surface tension, vapour pressure, of the solvent and the FWHM from the peaks shown in Fig. 3. The properties of the solvents used in this work were sourced from the CRC Handbook of Chemistry, 88th Edition, 2008. The surface tension was given for contact with air at 15 °C and 1 atm while both viscosity and vapour pressure are shown for 20 °C and 1 atm; the eccentricity was calculated by dividing the maximum and minimum ellipse axis length from the scattering patterns in Fig. 2. The scattering vector value, *q*, and corresponding space scatterer dimension, *d*, are given for comparison.

Solvent	Eccentricity	q^b ($Å^{-1}$)	d^b (nm)	FWHM (°)	Dipole moment (Debye)	Viscosity (mPa s)	Surface tension (mN/m)	Vapour pressure (kPa)
DIW	1.9	0.0632	9.93	48.5	1.85	0.89	72.8	3.17
THF/DMF	1.25[a]	0.06721	9.34	53	–	–	–	–
Acetone	1	0.06321	9.93	70	2.91	0.306	25.2	30.8
IPA	1.1	0.06454	9.73	74	1.66	2.038	23	6.02
DMF	1.5	0.06188	10.14	77	3.86	0.794	35.74	0.439
THF[a]	N/A			N/A	1.63[a]	0.456[a]	26.4[a]	21.6[a]
CNT forest ref.	8.50	0.0738	8.50	120				

[a] THF was used only as a modifier to DMF (mixed at 10:90).
[b] The mean size of the scatters *d* was calculated from the main peak corresponding to the CNT outer diameter and was calculated following Eq. (1) in the S.I.