VERTICALLY ALIGNED CARBON NANOTUBES: FROM NANOSCALE SELF-ORGANIZATION TO MACROSCALE PRODUCTION AND APPLICATION

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Carbon nanotubes (CNTs), which are cylindrical tubes consisted of wrapped graphene sheets, possess extremely high tensile strength, high modulus, large aspect ratio, low density, good chemical and environmental stability, and high thermal and electrical conductivities. Various applications based on CNTs have been demonstrated. However, it is noticed that the agglomerated CNTs showed limited improvement on products, and the extraordinary performance of CNTs were not fully illustrated. The alignment of CNTs greatly affects the performance of CNT in macroscopic applications. If the CNTs can be aligned to form ordered CNT arrays, the as-grown arrays can be directly used as nano-spring, anisotropic conductive materials, multi-functional membranes, filters, battery electrodes, and field emitters. Super aligned CNTs can also be further processed into strong fibers, transparent conductive films, electronic components, and high-performance composites. Even with the loss of the original alignment, longer and straighter multi-walled CNTs from the aligned CNT arrays are found to be better than randomly aggregated multi-walled or even single-walled CNTs in improving the electrical, mechanical and thermal properties of a polymer. Vertically aligned CNT arrays were one of the advanced materials to demonstrate the fascinating properties of nanomaterials.

Up to now, many intriguing applications based on aligned CNTs have been proposed. However, not all of them are with clearly practical prospects. The major reason is that the availability of aligned CNTs in large amount is still very limited. Usually, expensive silicon wafers were used as the growth substrate, and only several milligrams of aligned CNT samples can be obtained in a batch of chemical vapor deposition. The price of aligned CNTs was estimated to be 2,000 U.S. dollars/piece. If the goal of nanotechnology were for human benefit, one of the urgent tasks is the ability for mass production of high quality CNT arrays. Exploring the science and developing the technology for industrial production of aligned CNT arrays becomes one of cutting-edge issues in chemical engineering. In this thesis, the scientific problems of aligned CNT growth are discussed, and the mass production of aligned CNT arrays is analyzed by nanoscale process engineering methods. Based on the novel scientific understanding, a practical route to the mass production of aligned CNT arrays is proposed and realized to promote the applications of aligned CNTs.

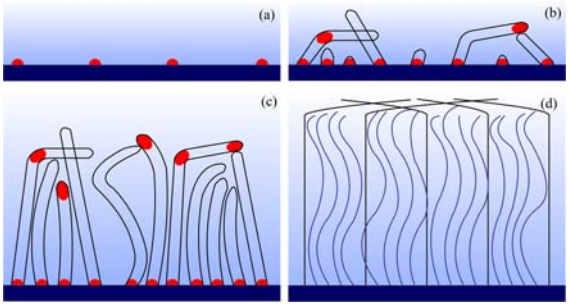

Fig. 1 Schematic description of the synchronous growth of CNT array: (a) Catalyst formation, (b) CNT nucleation and CNT random growth on the substrate and a woven structure formed after a period of growth, (c) CNTs now cannot grow freely on the surface due to horizontal and vertical resistance and stress created by the interactions between upward growing later formed Type 2 CNTs and the earlier formed Type 1 CNTs that comprised the woven structure. (d) Synchronous growth of long CNT array with pristine stress [1].

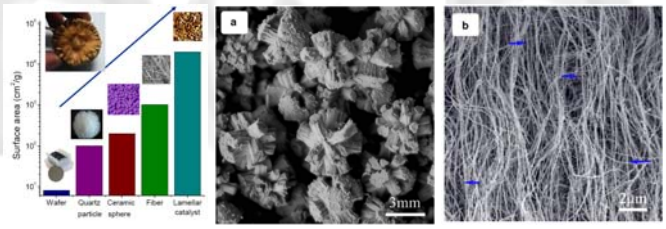

Fig. 2 Left: To increase the amount of aligned CNT growth, various kinds of particles with high surface area were used as substrate; Right: (a) Large amounts of aligned CNT array grown at 800 ^{o}C on sphere; (b) SEM of the aligned CNTs in (a). Type 1 (straight, the arrow pointed CNTs in (b)) and Type 2 (curved) CNTs were shown in the aligned CNT arrays [2].

Based on the understanding of CNT array structure, the growth mechanism of CNT arrays was proposed. On the atomic scale, the vapor-liquid-solid model explains how a single CNT grows out from the catalyst, and the diameter of CNTs in the arrays can be easily modulated through nucleation and sintering of the metal catalyst particles during the heterogeneous catalysis process. The growth sites of individual CNTs in the array were at the bottom of the array. To illustrate the synchronous growth of CNTs, a multi-layered CNT arrays grown by a four-step interim reactant supply reaction were characterized by the scanning electron microscopy and Raman spectra. They were used to deduce that the

pristine stress was present in the CNT arrays. A model of the stresses caused by space limitation and different growth rates was used to explain the development of a synchronous growth of the CNT arrays [1]. Large amount of CNTs were self organized into array structure based on the interaction among CNTs, which can be described by the Onsager virial theory. The CNT arrays can be easily synthesized on a low curvature substrate with high density active metal particles. Spinnable CNT arrays, as well as super-long CNT arrays with a length of 14.5 mm, were obtained *via* the floating catalyst chemical vapor deposition.

To overcome the limited surface area for the growth of CNT arrays on flat substrates, radial growth of CNT arrays on the surface of various particles was proposed [2]. Large amount of CNT arrays can radially grow on spherical, flaked, and fibrous particles. For example, multi-walled CNTs in array form with a diameter of 10-50 nm and a length of 10-2,000 μm were radially synthesized on ceramic spheres. Double-walled CNTs in array form with a diameter of 4-7 nm and a length of 50 μm were grown on FeMgAl layered double hydroxide flakes.

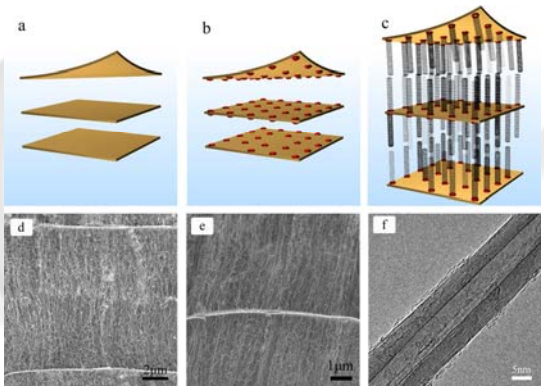

Fig. 3 (a-c) Illustration of the formation of intercalated growth of VACNT films into layered inorganic compounds; (d, e) SEM images of aligned CNTs. (f) TEM image of a multi-walled CNT [3].

To avoid the damage caused by the collisions among CNT arrays during the process of transport and fluidization, a strategy of intercalated growth of CNT arrays among layered catalyst was proposed. The layered vermiculite catalyst with dispersed active particles among the layers was prepared by ion-exchanged method. Vertically aligned CNT arrays with a diameter of 7-13 nm and a length of 0.10-100 μm, were intercalated among inorganic layers.

Large amount of CNT arrays can be produced in a fluidized bed with the layered catalyst [4]. A 3.0 kg/hr CNT array productivity was realized in a fluidized bed reactor with a diameter 500 mm. The CNTs in the as grown arrays were with good alignment, and can be easily purified. A chemical process for mass production of functional CNT arrays was demonstrated [5].

Fig. 4 The pilot plant facility for VACNT array production at a rate of 3.0 kg/h [5].

The introduction of strong yet flexible CNTs made the self-organized 25 μm CNT arrays intercalated composites highly compliant and resilient, in contrast to bare inorganic compounds that are rigid and brittle. The CNT-intercalated composite can be repeatedly compressed at high strains, with an energy absorption capacity of 149 kJ/kg, which is much higher than CNTs in cushioning polystyrene foams (36 kJ/kg). The enhanced mechanical properties are due to the combination of aligned CNTs with inorganic layers. The CNTs still kept good alignment after 20 cycles of compression. The obtained aligned CNT arrays intercalated composites are with superior mechanical properties as energy absorption, dumping, shock absorbing materials, which are highly necessary for aircraft, container, car, and so on. Applications of CNT arrays as energy-absorbing materials, buckypaper, transparent conductive film, composites for energy conversion were also explored.

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