In Situ Assembly of Multi-Sheeted Buckybooks from Single-Walled Carbon Nanotubes

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ABSTRACT We report a simple approach for the direct and nondestructive assembly of multi-sheeted single-walled carbon nanotube book-like macrostructures (buckybooks) with good control of the nanotube diameter, the sheet packing density, and the book thickness during the floating catalytic growth process. The promise of such buckybooks is highlighted by demonstrating their high capacitance and high-efficiency molecular separation by directly using them as a binder-free electrode and as a filter, respectively. Our approach also provides a flexible and reliable way to easily assemble various other types of nanotubes into book-like or even more sophisticated sandwich-like hybrid macrostructures, realizing the shape-engineering of one-dimensional nanostructures to macroscopic well-defined architectures for various applications.

KEYWORDS: carbon nanotubes · assembly · macrostructure · floating catalyst · filtration

Individual carbon nanotubes (CNTs) show great promise for a wide range of applications because of their unusual structural, mechanical, thermal, and electrical properties.[1−3] On the other hand, the building and organization of macroscopic CNT-based architectures are equally important in order to realize the full potential of CNTs with unique functionality in integrated systems.[4,5] As a result, various well-defined configurations such as ribbons,[6] yarns,[7] forests,[8] fibers,[9] membranes,[10] films,[11] buckypaper,[12] sheets,[13] brushes,[14] foams,[15] solid,[16] wafers,[17] and adhesives[18] have been fabricated. Each form has its unique functionality and special applications. For example, the fascinating chemical and physical properties of two-dimensional (2D) paper-like CNT macrostructures (including buckypaper, sheets, films, membranes, and so on) give them tremendous potential as functional elements or structural components in various applications such as energy storage,[19] nanocomposites,[20] chemical separations,[21] biomedicine,[22] optoelectronics,[23] electronics,[24] *etc*. The existing methods to fabricate macroscopic paper-like materials mainly involve various post-treatment techniques such as drop drying,[25] spraying,[26] purification and functionalization,[27] spin coating,[28] liquid-phase filtration,[29] and blown film extrusion.[30] However, these methods suffer severe limitations in terms of product quality or production efficiency because (i) the quality of the resulting macrostructures strongly depends on the pristine CNTs that normally vary sharply in diameter and chirality;[31−33] (ii) before dispersion in liquid media with surfactants for fabricating such macrostructures, the pristine CNTs are required to be well purified, normally using strong acids followed by oxidation in air, which may not only damage and contaminate the CNTs but also leave chemical waste behind;[11,12,25−31] and (iii) releasing of free-standing paper-like macrostructures needs to dissolve the filtration membrane in wet chemicals or to directly peel the macrostructures off the filtration membrane,[11,12,30,31] which may further damage the resulting products.

The important difference of our approach from the above post-treatment techniques is that single-walled CNTs (SWNTs) with uniform and tunable diameters are directly assembled into macroscopic 2D thin sheets with uniform and tunable thickness and then into novel 3D multi-sheeted book-like macrostructures (buckybooks) when SWNTs are grown by floating catalyst chemical vapor deposition (FCCVD) that has been used to synthesize CNTs[34] and other carbon nanostructures.[35,36] Owing to no damage to SWNTs in this *in situ* assembly process, the as-fabricated buckybooks can maximally retain the intrinsic properties of individual SWNTs such as high mechanical flexibility, selective adsorption, and excellent electrical conductivity. This is the

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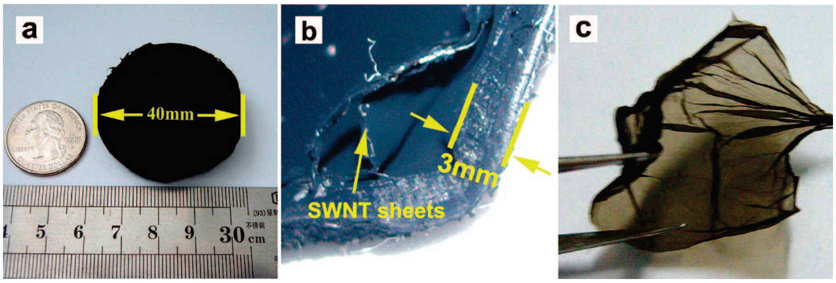

Figure 1. Photographs of a buckybook of (a) ~40 mm in diameter and (b) ~3 mm in thickness, and (c) a freestanding SWNT monosheet peeled from a buckybook with tweezers.

key advantage over the existing post-treatment methods to make paper-like CNT macrostructures.

Figure 1a,b shows a typical example of the as-fabricated buckybook of ~40 mm in diameter and up to 3 mm in thickness after a reaction time of ~30 min. Freestanding monosheets can be peeled off from the buckybooks. The homogeneity of the peeled monosheet is good enough to be optically transparent (Figure 1c) because if the sheet is not very homogeneous, due to the severe diffusion, it will lose high transparency even though it is thin enough. In contrast, derived from the ancient art of paper-making, the most commonly used solution-filtration technique is a rather slower process (*i.e.*, typically a week-long filtration of CNTs dispersed in the solution at room temperature) and normally only produces a monolayer sheet in one batch.[13] Most importantly, the buckybooks can be easily engineered: the final thickness of the buckybooks is controlled directly by reaction duration time; the size of the buckybooks can be scaled up simply by using a larger reaction quartz tube, and the "content" of the buckybooks, that is, the diameter of individual SWNTs and the packing density of SWNT sheets, can be finely tailored by changing the synthesis parameters.

Scanning electron microscope (SEM) observations further confirm the well-defined structure of the buckybook, which consists of several hundreds of homogeneous thin monosheets (Figure 2a−c). Figure 2d exhibits a very clean, transparent, and smooth surface of a monosheet peeled from the buckybook. The sheet consists of numerous compactly inter-entangled SWNT bundles (Figure 2e) and is ~500 nm thick (Figure 2f). In fact, the interaction between SWNT bundles is so strong that the sheets can well keep their intactness even after ultrasonication for a long time in ethanol, which demonstrates a high mechanical flexibility of the sheets. The thickness of a monosheet in the buckybooks is closely related to the dispersion concentration of SWNTs in the carrier gas during the FCCVD synthetic process, which in turn is determined by the growth rate of SWNTs and the flow velocity of carrier gas. Generally, higher carbon feeding rates, higher sublimation temperatures (T_{sub}) of ferrocene, and lower flow rates of carrier gas can increase the sheet thickness of buckybooks, as shown in Figure 3.

Transmission electron microscope (TEM) investigations (Figure 4a) demonstrate that the nanotubes were high-quality SWNTs, with the SWNT percentage of over 95% among the tubular objects. The inset in Figure 4a exhibits a perfect hexagonal packing structure in the cross section of a SWNT bundle, suggesting that the

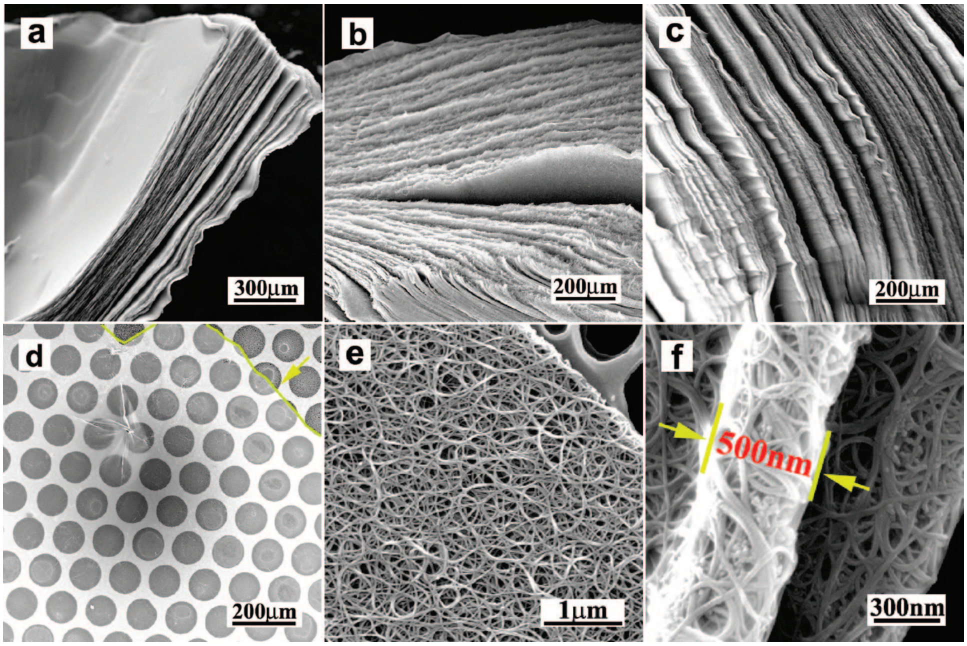

Figure 2. SEM images of (a) the top, (b) side, and (c) cross-section of a SWNT buckybook. (d) Low-magnification SEM image of a peeled SWNT monosheet that was placed on a copper grid and (e) high-magnification SEM image of the same monosheet with a monolayer of (f) ~500 nm in thickness, exhibiting abundant entangled SWNT bundles with clean surfaces.

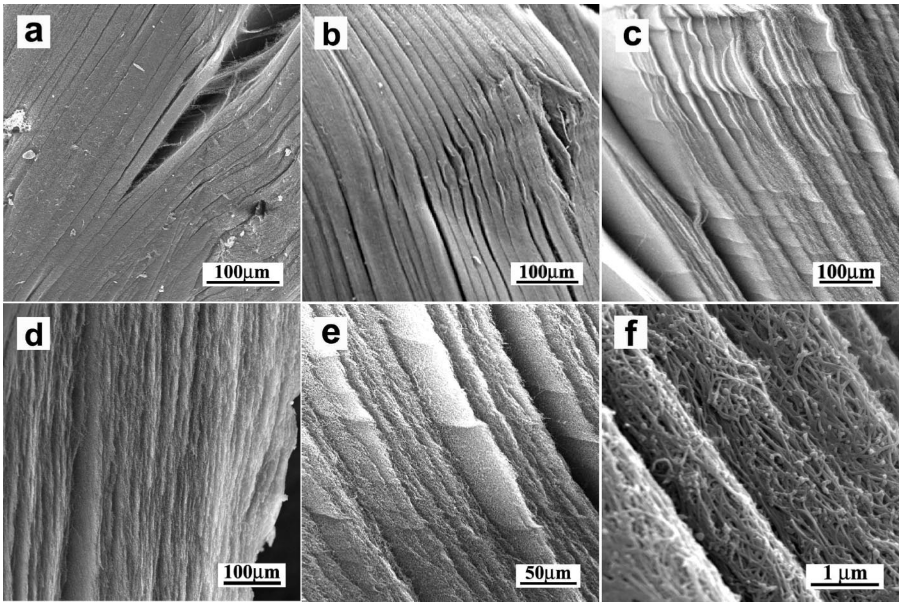

Figure 3. SEM images of the buckybooks with different sheet thicknesses synthesized under different conditions: (a) T_{sub} of 120 °C, 1000 sccm H_2 flow rate, and 100 sccm CH_4 flow rate; (b) T_{sub} of 120 °C, 1000 sccm H_2 flow rate, and 60 sccm CH_4 flow rate; (c) T_{sub} of 120 °C, 1000 sccm H_2 flow rate, and 15 sccm CH_4 flow rate; (d) T_{sub} of 90 °C, 1000 sccm H_2 flow rate, and 6 sccm CH_4 flow rate; (e) T_{sub} of 90 °C, 2000 sccm H_2 flow rate, and 6 sccm CH_4 flow rate; and (f) T_{sub} of 70 °C, 2800 sccm H_2 flow rate, and $\leq$2 sccm CH_4 flow rate.

bundle consists of uniform SWNTs. Measured from high-resolution TEM (HRTEM) images, the diameter distribution of ~82% SWNTs is found in a narrow range of 2.1 ± 0.2 nm, with a Gaussian mean value of ~2.1 nm (Figure 4b). Moreover, the almost identical Raman spectra (Figure 4c) with only one narrow peak in the ra-

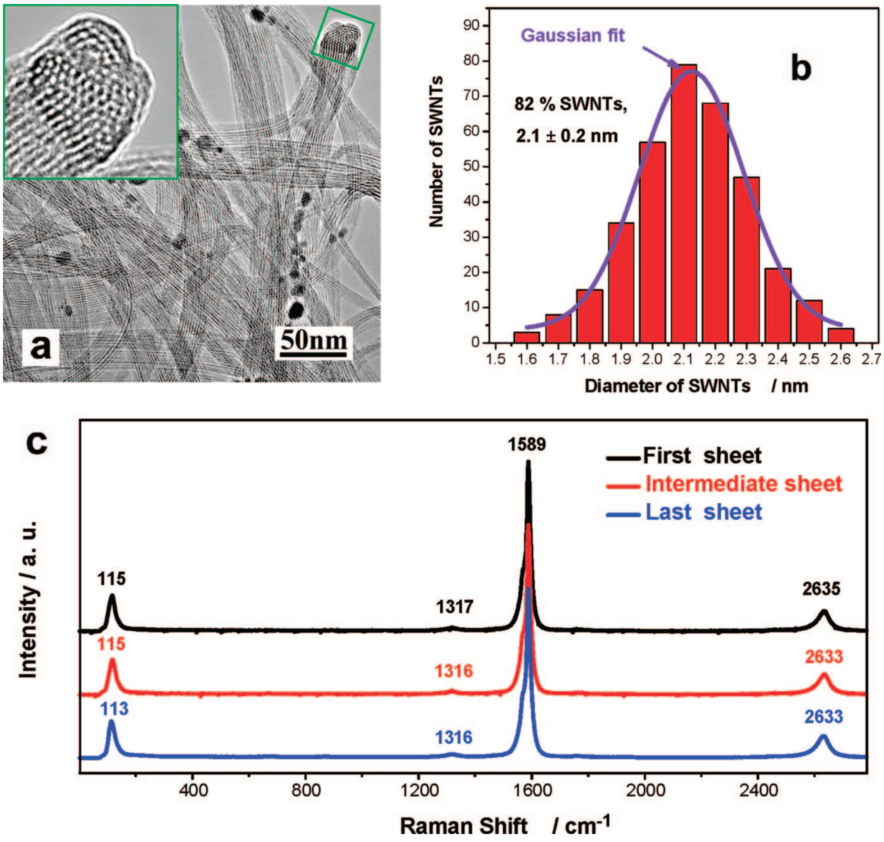

Figure 4. (a) TEM image of a typical SWNT sheet comprising high-quality SWNT bundles. Inset: a perfect hexagonal packing structure of a SWNT bundle. (b) Diameter distribution of the SWNTs with a Gaussian mean value of ~2.1 nm. (c) Raman spectra of the first (black line), intermediate (red line), and last (blue line) individual SWNT sheets through the thickness of the buckybook, showing the high structural homogeneity of the SWNTs in the buckybook.

dial breathing mode (RBM) region and a small intensity ratio of D-to-G band strongly indicate that the sheets throughout the thickness of the buckybook are composed of high-quality SWNTs with high structural homogeneity. From the RBM frequency,[37] the diameter of the SWNTs was estimated to be ~2.2 nm, well in agreement with the above HRTEM statistic results, demonstrating that the growth and assembly of SWNTs in the FCCVD process are almost identical during the whole reaction duration time.

As mentioned above, the post-treatment techniques to make paper-like CNT macrostructures usually involve the dispersion of CNTs with a surfactant in aqueous solutions, and therefore the contacts in the resulting sheets are weak, which makes such materials to have relatively low mechanical strength and poor electrical conductivity. In stark contrast, owing to the long persistent lengths of SWNTs with extremely good rigidity, the newly formed SWNTs floating in the high-velocity gas flow can gain maximal overlapping and interpenetration when they are forming networks that can yield excellent mechanical integrity and electrical conductivity.[11] In addition, since the microstructure of SWNTs is only determined by the growth conditions but independent of the assembly processing, individual SWNTs with different diameters or semiconducting/metallic electrical properties can be finely tailored and tuned by changing the growth conditions of the SWNTs for the subsequent assembly of the buckybooks.[37] For example, the sheet resistance of the SWNT sheet containing more metallic nanotubes is ~4.3 Ω/square, nearly 5−20 times lower than that of the counterpart enriched with more semiconducting nanotubes. With the excellent electrical conductivity, high mechanical flexibility, and special densified geometry, the SWNT buckybooks are expected for applications in compact energy storage in confined spaces such as mobile phones and satellites;[16] for example, as an ideal binder-free SWNT electrode for supercapacitors, the buckybooks show a promising high capacitance of ~100 Fg^{-1}, while keeping an excellent power output at fast current loading, which is extremely important for compact high-power-density cells (Figure S1, Supporting Information).

Moreover, our approach can be easily extended to assemble various other types of 1D nanostructures such as double-walled CNTs, multi-walled CNTs (MWNTs), or other inorganic nanotubes that can be produced by FCCVD into thin sheets, thick books, or even sophisticated sandwich-like hybrid architectures with different functional layers. For instance, an example of a sandwich-like SWNT/MWNT/SWNT buckybook of ~9 mm in thickness was obtained by simply varying the sublimation temperature of ferrocene (Figure S2, Supporting Information).

Although theoretical predictions using CNTs for chemical separations have been verified experimentally,[38−40] building CNT-based membranes with good control of the geometry, density, and dimension for chemical separations still remains a great challenge. The nice features of the buckybooks should find a practical application of CNTs in chemical separations, particularly given the inter-tubular spaces (nanoporosity) of individual monosheets and the selective adsorption properties of SWNT surfaces.[41] Nowadays, even the state-of-the-art water treatment facilities may be still far from natural-law limits in their ability to separate compounds, remove chemical agents, transport water molecules, and move ions against concentration gradients. For instance, chemically treating the total volume of water to transform or remove a specific trace micropollutant class (*i.e.*, organic compounds, pharmaceutical derivatives, agricultural chemicals, and so on) is usually expensive and potentially itself harmful.[42] It is known that methyl orange (MO), rhodamine B (RhB), and methylene blue (MB) are the most commonly used coloring agents, representing some of the principal pollutants in textile industry.[43] For demonstration, we performed the vacuum filtration of low-concentration MO, RhB, and MB as target pollutants in aqueous solutions (*i.e.*, $\sim 4 \times 10^{-5}$ mol/L) and found that the buckybooks as a filter completely eliminated these dyes from water.

Before filtration, the as-fabricated buckybooks were first treated in the concentrated sulfuric acid for removal of metal impurities (Figure S3, Supporting Information). Meanwhile, after such treatment, the surface of buckybooks became superhydrophilic, which benefits the improvement of mass transport in the filtration process. Figure 5a schematically shows a buckybook mounted to a homemade filtration setup for the vacuum-filtering process. Driven by a pressure difference of ~ 0.1 MPa, the flow rate of aqueous solutions ranges between 5 and 30 mL h^{-1} cm^{2}, depending on the SWNT packing density and the thickness of the buckybook filter. After filtration, all filtrates became very clean without any colors (Figure 5b), indicating complete elimination of these dye pollutants from water. UV−vis spectra were further used to measure the filtered and unfiltered solutions through the buckybook filter. It was found that all typical UV−vis absorption bands of MO (463 nm), RhB (553 nm), and MB (663 nm) completely disappear for these filtrates (Figure 5c), demonstrating the high removal capacity of the buckybooks for the dye molecules from water. Owing to the highly selective adsorption properties of SWNT surfaces and the nanoscale inter-tubular spaces of individual monosheets that match the size of the target molecules, the buckybook filters allow molecular sieving and forced interactions with chemically selective molecules bound to the SWNT surface and the inter-tubular spaces. The filtration mechanism of the buckybook filters through the intertubular spaces of SWNTs should be different from that of the tip-opened aligned CNT membranes by using

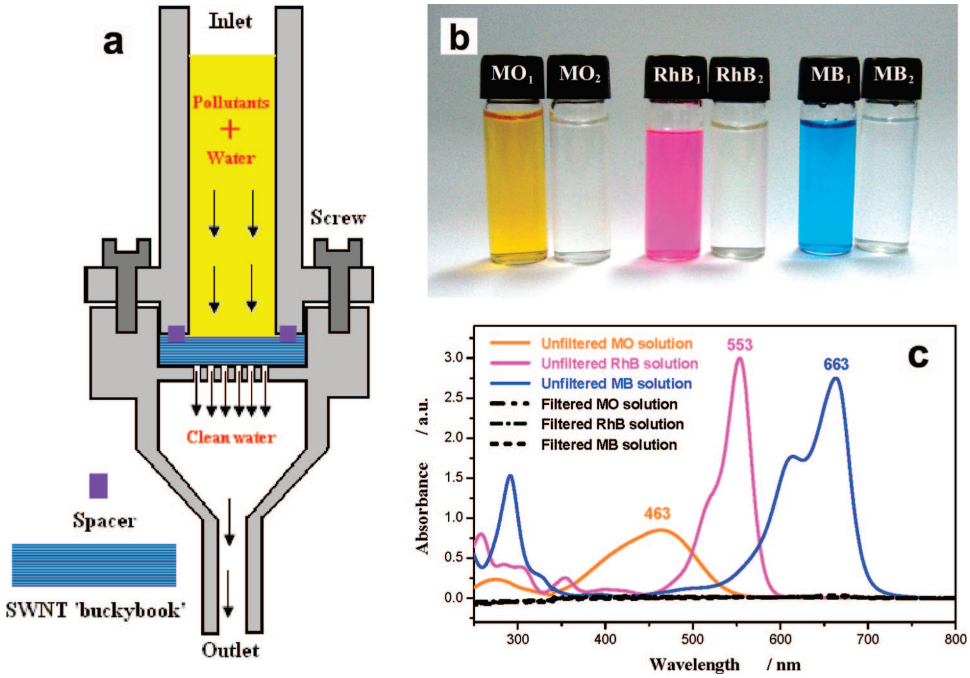

Figure 5. (a) Schematics of the filtration setup used for molecular separation. (b) Photograph of the pristine solutions (MO_1, RhB_1, and MB_1) and the corresponding filtrates (MO_2, RhB_2, and MB_2). (c) UV−vis spectra of the unfiltered and filtered MO, MB, and RhB samples.

the internal channels of nanotubes that may be easily plugged during filtration process.[10]

The buckybook filters can be easily cleaned repeatedly with purging cycles after each filtration process to regain their full filtering efficiency, while the reusability of conventional filters such as cellulose nitrate/acetate membranes is usually very poor after filtration. Besides the high removal capacity for organic molecules, the buckybook filters also possess a robust and strong structural integrity that can sustain water flow over weeks without any damage in our filtration process. Furthermore, owing to the high thermal, mechanical, and chemical stability of CNTs, an overwhelming advantage of the buckybook filters over conventional membrane filters is that they can be operated under various severe conditions including acidic, basic, corrosive, oxidizing, reducing environments, or elevated temperatures against wear and tear. Last but not the least, compared to the previous CNT-based filtration membranes with the filtering occurring in the inner channels of nanotubes,[10,38−40] the buckybook filters are easily manufactured and conveniently used in chemical separations. It is expected that, by controlling the microstructures and surface characteristics (*i.e.*, chemical functionalization) of SWNTs, the buckybook filters with high molecule-removal capacity and excellent reusability may be tailored to specific needs of chemical separations under any severe conditions.

In summary, we provide a simple and versatile approach for *in situ* fabrication of macroscopic 3D densified buckybooks of several millimeters in thickness by using a specifically designed porous substrate during the floating catalytic growth of SWNTs. The SWNT diameter and the sheet packing density in buckybooks can be finely tailored or tuned by changing the synthetic parameters. Owing to no damage to SWNTs in this *in situ* assembly process, the intrinsic properties of individual SWNTs are maximally retained in the buckybooks, which make our approach unique from other existing processes to make paper-like CNT macrostructures. The promise of such buckybooks was highlighted by demonstrating their high capacitance and high-efficiency molecular separation. Therefore, our findings represent a substantial progress toward realization of the shape engineering of 1D nanostructures to macroscopic structures with well-defined geometry, which is greatly advantageous for various practical applications.

METHODS

The synthesis and assembly of SWNTs were performed in a quartz tube reactor inside an electrical furnace. In order to build the buckybooks, a specifically designed porous membrane (made from various porous materials such as carbon fabric felt, gauze, *etc.*) with the same diameter as that of the inner diameter of the quartz tube reactor was used as a substrate, which was placed vertically at the outlet of the quartz reaction tube. In a typical experiment, 100−4000 sccm H_2 flow as carrier gas was introduced through the quartz tube. When the reaction temperature reached 900−1200 °C, a mixture of ferrocene/sulfur powder (S = 0.5−5 wt %) was sublimated at 50−120 °C and transported into the reaction zone by the gaseous flow. At the same time, 1−200 sccm CH_4 flow was introduced. When the SWNTs were continuously grown and formed in the reaction zone, they were immediately transported to the outlet end and *in situ* assembled into a buckybook on the specifically designed porous membrane. After growth, the furnace was cooled naturally to room temperature under the protection of the carrier gas.

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Supporting Information Available: Assembly of SWNT buckybooks with different monosheet thicknesses, assembly of sophisticated SWNT/MWNT/SWNT buckybooks, SWNT buckybook supercapacitors, and purification of SWNT buckybooks. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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