Fabrication of porous carbon nanotube network†

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We used the spin-coating method combined with ultrasonic atomization as a continuous, one-step process to generate a two-dimensional honeycomb network that was constructed from pure multi-walled carbon nanotubes.

Porous carbon materials are of substantial interest for various scientific and technical applications in electrochemical, catalytic, adsorbent, and gas-storage applications.[1] Most research efforts emphasize the use of templates and their subsequent removal to produce meso- and macro-porous carbons with controlled periodic open-framework. With this approach, a carbon precursor template from raw natural materials[2] (*e.g.*, wood, coal, petroleum pitches, and coconut shell) is first formed, followed by carbonization and then chemical leaching of the template materials. Such carbonization methodology is not straightforward, requiring multiple synthetic steps and long curing times.

Carbon nanotubes (CNT) are an excellent alternative as carbon precursors due to their high flexibility, specific surface area, low density, and superior optoelectronic characteristics.[3,4] Evaluating the potential of CNT as the basis of future nanotechnology, CNT-based conducting films pervade niche applications in flexible/foldable displays, touch screens, and transparent electrodes for liquid crystal displays.[5,6] However, to the best of our knowledge, creating a transparent conducting CNT texture with a porous framework has proven challenging. Here, we utilize the spin-coating method combined with ultrasonic atomization as a continuous, one-step process for the fabrication of quasi-honeycomb network built up of carbon nanotube wires.

Ultrasonic atomization uses a mist of micron-sized droplets from a humidifier. The droplets can be sprayed and deposited onto the surface of substrates where the water evaporates and dissolved substances react, precipitate, or decompose to form the product. This technique has allowed for the continuous, inexpensive production of micro- and nano-sized materials. Accordingly, a new micro-encapsulation method was performed by applying an ultrasonic atomizer to the pure multi-walled CNT (MWCNT) supernatant solution.[7,8] Fig. 1 shows that MWCNT suspendants have a tendency to form micro-encapsulated spheres 50 μm in size, which are deposited randomly on the polyethylene terephthalate (PET) substrate during the atomization process. The encapsulated spheres

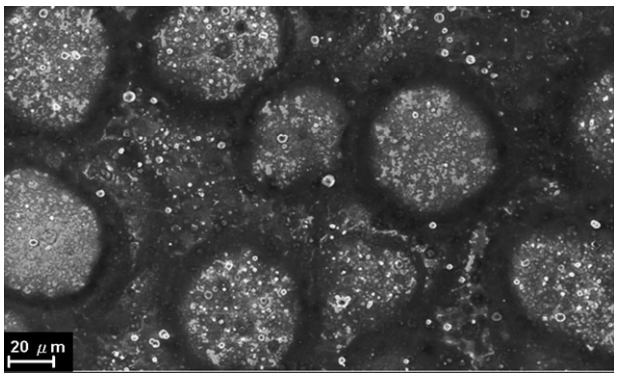

Fig. 1 FE-SEM image of CNT–SDS micro-encapsulated spheres self-aggregated onto a PET substrate.

comprised of individual CNT and sodium dodecyl sulfate (SDS) surfactant, acted a temporary template. After the SDS surfactant was partially washed away with water, field-emission scanning electron microscopy (FE-SEM) analysis of this representative film revealed that the CNT texture was formed from encapsulated particle shells *via* a "stick" mechanism, as indicated in Fig. 2. Like most prior methodology of self-organization, individual CNT "sticks" are attracted to each other through van der Waals interactions to form one-dimensional conducting wires. Also, the CNT wires have long persistence lengths and appear to become entangled to form intersecting points in the networks. Upon the removal of SDS completely, the surface topography of CNT texture shown in Fig. 3 reveals that a quasi-honeycomb framework was generated *in situ*.

This open-framework is unprecedented in the fabrication of CNT-related films. With regard to this honeycomb structure,

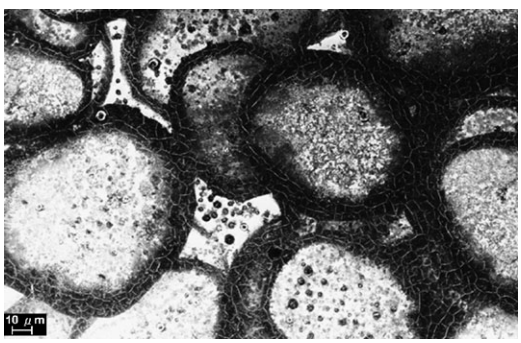

Fig. 2 FE-SEM image of formation of CNT texture, showing CNT conducting wires from "sticks" of individual CNT on the shell of micro-encapsulated spheres

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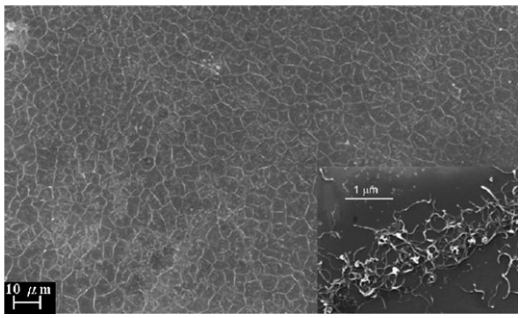

Fig. 3 FE-SEM image of the morphology of honeycomb networks constructed from pure CNT wires. Inset: one selected wall of CNT network.

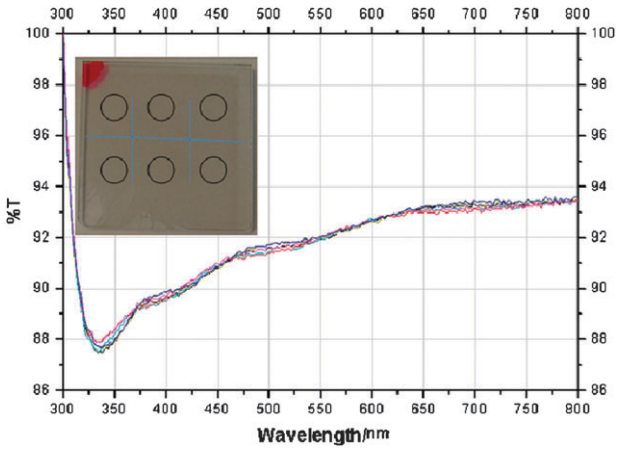

Fig. 4 UV-Vis spectra for the honeycomb CNT film, showing extra-transparency on the homogenous uniform film (4 × 4 cm^2). Selected six optical spectra on the circles were taken (Inset).

two intrinsic factors should prove beneficial for the fabrication of CNT films with both high transparency and good electrical conducting properties. First, the micro-scale open windows act as optical domains which have been recognized as an important factor to obtain the best optical transparency. Optical transmission measurements of the investigated CNT network were conducted with a Lambda 900 UV/Vis/NIR spectrometer (Perkin-Elmer Life and Analytic Science, USA). Fig. 4 shows that this level of porosity is consistent with its optical properties, with ultra-high film transmittance >85% over the visible part of the spectrum. Moreover, there is no difference on analysis of optical transmittance for this representative CNT film, indicating that the size of homogeneous honeycomb structure is up to 4 × 4 cm^2. Second, the distribution of the conducting sticks plays an important role in the electric properties of CNT networks. The larger the nanowire conductivity, the better the network conductance will be. The corresponding sheet resistance can reach 500 Ω sq^{-1} (using a four probe point stand equipment), comparable to single-walled CNT and indium tin oxide (ITO) onto PET substrate.[6]

In summary, porous carbon nanotubes frameworks have been achieved by the spin-coating method combined with ultrasonic atomization. This approach is straightforward for a large-sized film. Our work reveals that the honeycomb structure is an exceptionally important morphology to improve the electric conductivity, optical transmittance and thermal stability for carbon-based thin-film nanotechnologies. The conducting honeycomb CNT films should open new opportunities for the development of next-generation flexible touch screens.

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7 The CNT used in this work were grown by CVD methods. CNTs were purified according to the following procedure. 500 mg of CNT was heated in air at 400 °C for the removal of amorphous carbon and then was stirred in 500 mL HCl (6 M) for 3 h. The purified CNT were recovered by ultracentrifugation with deionized water. By repeating this process three times, TGA data shows that weight loss below 1 wt% at 600 °C indicated that the concentration of CNTs in the purified products reached as high as 99 wt% (Fig. S1, ESI†). We mixed 2500 mg L^{-1} CNTs (250 mg in 50 mL water) with 1% SDS surfactant concentrations and then sonicated the suspension using a high power tip sonicator for a very short time (3 min). The field-emission scanning electron microscopic (FESEM) images of CNTs films were obtained using Zeiss URTRA 55 field-emission scanning electron microscope. Moreover, Raman spectroscopy confirmed that CNT films are pure and well crystallized (Fig. S2, ESI†); the main D and G band appear at 1329 and 1580 cm^{-1}, respectively.
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