

Letter to the Editor

Three dimensional porous monoliths from multi-walled carbon nanotubes and polyacrylonitrile



A B S T R A C T

Three-dimensional (3D), porous monoliths with high electrical and thermal conductivities were produced by using unmodified multi-walled carbon nanotubes (CNTs) and polyacrylonitrile (PAN) as the starting compounds through a template-free thermally induced phase separation approach. Multi-walled CNTs in the PAN/CNT monoliths were fully dispersed and as a result, interconnected CNT networks with high uniformity were established. The average value of the porosity, surface area, electrical conductivity, thermal conductivity and mechanical strength were found to be 90%, 210 m²/g, 2.7 S/cm, 0.148 W/(m.K) and 1.1 MPa, respectively, for a 3D porous PAN/CNT monolith sample with a 33 wt% CNT loading. This new class of the CNT-based monolith opens up new possibilities for various practical applications.

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Three dimensional (3D) porous nanostructures are highly applicable for building up high-performance super-capacitors, fuel cells, batteries, filters, catalysts and the stationary-phases of chromatography [1–6]. The 3D porous nanostructures with carbon nanotubes (CNTs) as the frameworks are more advantageous, since higher surface areas and lower density can be easily achieved. A complicated post-treatment, however, is commonly required for obtaining high electrical conductivity and/or the thermal conductivity [7–9]. Dipping or coating a polymer based 3D substance using dispersed CNTs is a simpler method to obtain a CNT based 3D nanostructure; low stability and low loading efficiency have been the intrinsic difficulty and thus limited the practical application. A sol/gel polymerization method was able to produce a 3D porous nanostructure and the CNT loading as high as 55% was reported [7]; a further carbonization was still needed for obtaining a high value of electrical conductivity. CNTs used in previous studies, in most cases, have to be functionalized (chemically modified) via an oxidation treatment with strong acids as the oxidants [4]. The intrinsic conductive properties of CNTs can be largely damaged besides, scale-up for massive production is difficult to achieve.

It is demonstrated experimentally in this study that a CNT based 3D porous nanostructure having high electrical/thermal conductivity, mechanical strength together with a large surface area is obtainable by using unmodified multi-walled CNT as conductive frameworks and polyacrylonitrile (PAN) as the polymer precursor via a monolith approach. We selected PAN because of its high thermal and electrical stability, good mechanical properties, durability, melting point, and low cost [10]. We determined that the thermally-induced phase separation (TIPS) [1] is the simplest and most effective method for developing the desired CNT/PAN based

monolith. TIPS is a template-free method for which the shape of the CNT-based 3D porous monolith can be designed at well.

Multi-walled CNTs were dispersed in dimethyl sulfoxide (DMSO) at the tubular level of dispersion using a cholate/fluro-surfactant mixture as the dispersant and polyvinylpyrrolidone as the stabilizer. The degree of CNT dispersion was confirmed by a series of size distribution analyses followed by the morphology observations using SEM. A typical SEM image of a tubular level CNT dispersion in DMSO is given in Supporting information Figure S1. A small amount of deionized water was added into the DMSO containing the multi-walled CNT being dispersed at the tubular level of dispersion; this mixed solution was then used to dissolve PAN for developing the 3D porous monoliths (the detailed experimental protocol is given in Supporting information section 1). In this study, we mainly focused on enhancing the electrical conductivity, thermal conductivity, and surface area of the CNT/PAN monolith. Therefore, we optimized the important parameters that affected the formation and properties of the CNT/PAN monolith, such as the PAN concentration, the CNT concentration, and the volume ratio of the DMSO/water and the degree of the dispersion for the CNTs, etc.

Generally, in TIPS the temperature triggers the polymer-diluent system to undergo either a liquid-liquid or solid-liquid separation, depending on the polymer-diluent interaction [9]. In the PAN-DMSO system, a strong dipole-dipole interaction exists between the nitrile ($-C\equiv N$) group of PAN and the sulfinyl ($O=S$) group of DMSO. A miscible liquid can be obtained by dissolving PAN in DMSO with heating at high temperature. Upon cooling, this PAN/DMSO system solidifies via crystallization at a relatively low temperature. However, no phase separation is possible because of the

strong PAN/DMSO interaction, but in the presence of water in a suitable ratio a solid-liquid phase separation can occur, while cooling the hot homogeneous mixture [1,9].

Pure PAN monolith fabrication was possible within the concentration range of 5–12 wt% of PAN and 85–90% volume of DMSO. If the PAN concentration was below 5%, monolith fabrication was impossible because of the insufficient number of PAN molecules. Higher concentrations of PAN increase the viscosity of the mixture, so that the diluent molecules can be fixed at an adjacent nucleus prior to agglomeration, which affects the crystal growth [1,9]. In the PAN/CNT composite monolith preparation, the conditions differed because the viscosity of the CNT dispersion was higher than often when using pure DMSO. In a typical synthesis we dissolved 6wt% PAN in a 13/87% volume ratio of the water/CNT-DMSO dispersion. The CNT loading rate for the CNT/PAN monolith varied between 7.5 and 35 wt% based on the PAN concentration.

We confirmed that CNT aggregation did not occur during monolith fabrication by dynamic light scattering (DLS) analysis at each step during the fabrication. The mean particle size of the initial CNT dispersion in DMSO was 88 nm. Maintaining the same size distribution in the subsequent two steps was extremely challenging. In our observation, we understood that the surfactant played a key role in achieving an appropriate dispersion [11]. The experimental proof given in Supporting information Figure S2, showed the same mean particle size as the original CNT dispersion (initial), the CNT dispersion mixed with water (intermediate), and after complete dissolution of PAN in the CNT/DMSO/water mixture (final). This analysis was very important because the aggregation of CNT reduces the conductivity of the CNT/PAN composite monolith.

Detailed observations of the CNT/PAN composite monolith were carried out with a scanning electron microscope (SEM) and the highly magnified images are depicted in Fig. 1. From Fig. 1a, we concluded that the cross-linked polymerization, as well as the 3D fabrication of PAN, was obtained. A continuous interconnected porous structure with a pore size between 0.6 and 1 μm was obtained. This interconnected PAN skeleton was also the key element for immobilizing CNTs in the CNT/PAN monolith. CNTs were firmly

being linked and the CNTs formed a continuously interconnected network that developed inside the PAN/CNT composite, as was clearly visible (Fig. 1c and d.)

In this template-free approach, the PAN polymer itself acted as the binder, as well as the mold for the CNTs. We thus demonstrated an effective method for the fabrication of the CNT based 3D monolith in various shapes and sizes (Fig. 1b) by utilizing our advanced technique. We prepared a thin 3D monolith film having a thickness of less than 100 μm by simply coating the PAN/CNT colloidal solution on a glass surface. The length and breadth of the thin film was more than 25 cm and 13 cm, respectively. In addition, the cylindrical monolith of different sizes thus confirmed that the 3D fabrication was not limited to thin/thick films. This achievement can be considered as an important breakthrough in the CNT based 3D monolith fabrication.

The X-ray diffraction (XRD) patterns of the sole PAN monolith and the PAN/CNT composite monolith are shown in Supporting information Figure S3. In both PAN and the PAN/CNT composite monolith XRD pattern strong diffraction peak at a 2theta value of 16.71° which indicates the presence of an ordered lamellar phase (010 plane) for the PAN molecules (JCPDS No: 048-2119). Also, broad peaks at 25.58° and 29.36° which arise due to the disordered phase in the PAN intramolecular chain arrangement corresponding to the 210 and 300 planes, respectively. A diffraction peak at 25.92° in the PAN/CNT composite monolith XRD pattern clearly indicates the 002 reflection of the lamellar carbon structure in the composite monolith (JCPDS No: 058-1638) [1].

The presence of PAN in the PAN/CNT composite monolith was analyzed by FTIR spectroscopy (Fourier Transform Infrared spectroscopy), data are given in Supporting information Figure S4. The characteristic nitrile peak ($\text{C}\equiv\text{N}$ stretching mode) is located at wave number 2250 cm^{-1} . C–H bending and C–H stretching of the alkane group were observed at 1458 cm^{-1} and $2866\text{--}2935\text{ cm}^{-1}$, respectively. The band around 3500 cm^{-1} is due to O–H stretching of the water molecule [12].

The nitrogen adsorption/desorption isotherm of the PAN/CNT composite monolith followed a type IV isotherm is shown in

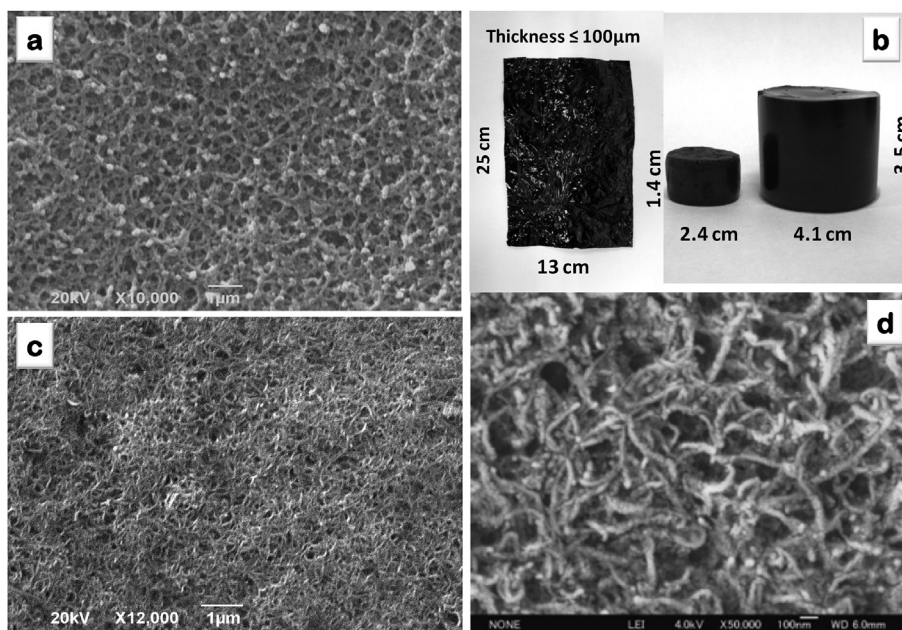


Fig. 1. a) Cross-sectional SEM image (magnification 10,000x) of pure PAN monolith, b) digital image of the PAN/CNT monoliths of different shapes and sizes, c) cross-sectional SEM image (magnification 12,000x) of a CNT/PAN composite monolith and, d) high magnification (50,000x) of the CNT/PAN composite monolith. (A colour version of this figure can be viewed online.)

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