**Three Dimensional Porous Monoliths from Multi-Walled Carbon Nanotubes
and Polyacrylonitrile**

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Abstract

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 entire elements 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%, 210m²/g, 2.7S/cm, 0.148W/(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.

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, 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 template-free method with 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 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 analysis followed by the morphology observations using SEM. A typical SEM image of the tubular level CNT dispersion in DMSO is given in [supporting information Figure S1](#). A small amount of deionized water was added into 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 (detailed experimental protocol is given in [supporting information section 1](#)). In this study, we mainly focused on the 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 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 7.5-35 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 88nm. 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 in 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 [Figure 1](#). From [Figure 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 0.6-1 μ m was obtained. This interconnected PAN skeleton was also the key element for the immobilizing CNTs in the CNT/PAN monolith. CNTs were firmly being linked and formed a continuously interconnected network that developed inside the PAN/CNT composite, was clearly visible ([Figure 1c](#) and [Figure 1d](#).)

Figure 1. a) Cross-sectional SEM image (magnification 10000x) of pure PAN monolith, b) digital image of the PAN/CNT monoliths of different shapes and sizes, c) cross-sectional SEM image (magnification 12000x) of a CNT/PAN composite monolith and, d) high magnification (50,000x) of the CNT/PAN composite monolith.

In this template-free approach, the PAN polymer itself acted as the binder, as well as the mold for CNT. We thus demonstrated an effective method for the fabrication of the CNT based 3D monolith in various shapes and sizes (Figure 1b) by utilizing our advanced technique. We prepared a thin 3D monolith film having a thickness of less than 100 μ m by simply coating the PAN/CNT colloidal solution on a glass surface. The length and breadth of the thin film was more than 25cm and 13cm, 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 indicate the presence of an ordered lamellar phase (010 plane) in the PAN molecule (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 plane respectively. A Diffraction peak at 25.92° in the PAN/CNT composite monolith XRD pattern clearly indicate 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 ($C\equiv N$ stretching mode) is located at wave number 2250cm^{-1} . C-H bending and C-H stretching of the alkane group were observed at 1458cm^{-1} and $2866\text{-}2935\text{cm}^{-1}$ respectively. The band around 3500cm^{-1} is due to O-H stretching of water molecule [12].

The nitrogen adsorption/desorption isotherm of the PAN/CNT composite monolith followed a type IV isotherm ([Figure 2a](#)). The BET (Brunauer, Emmett and Teller) surface area of the pure PAN monolith varied from $160\text{-}180\text{m}^2/\text{g}$, exactly as known from the literature [1]. In addition, the surface area of the PAN/CNT composite monolith was between $210\text{-}240\text{m}^2/\text{g}$ with a mean pore diameter 5-6 nm, which is much improved over the pure PAN monolith. The composite monolith also displayed remarkable 90-95% porosity. The high porosity made the PAN/CNT composite monolith lighter than water so that the structure can float on the surface of water ([Supporting information Figure S5a](#)). The average bulk density of the composite monolith was $0.8\text{g}/\text{cm}^3$. The composite can absorb 13 times its own weight of water, and then completely regain its original state upon drying. This reversible nature enhances the potential applications of this composite in water treatment and absorption research. It is worth noting that while the PAN/CNT monolith exhibits a high porosity and a very low density value, although the material possesses high mechanical strength between 1.1-1.5 MPa such that it can support *ca.* 20,000 times its own weight, as shown in [Supporting information Figure S5b](#).

Figure 2. a) Nitrogen adsorption (A) and desorption (B) isotherms of a PAN/CNT composite monolith and b) Thermograms (TG) of the PAN/CNT composite monolith in air and nitrogen atmospheres.

We evaluated the thermal stability of our monolith in both an inert atmosphere and in the presence of oxygen. [Figure 2b](#) displays the thermal behavior of the PAN/CNT composite monolith. The major thermal reaction processes were stabilization, carbonization, and graphitization, depending on the heating conditions[13]. The stabilization occurred between 250-350°C in both inert atmospheric conditions and in the presence of oxygen. The important reactions occurring in the stabilization process were oxidation, dehydrogenation, and cyclization. An exothermic process accompanied the conversion of a triple bond structure into a double bond structure, resulting in a six-membered cyclic ring. A weight loss of 15-20 % was observed during stabilization due to the evolution of the gaseous products of nitrogen and hydrogen [13]. When the temperature rose to 600°C, carbonization occurred under inert conditions. The cyclic structures then underwent further dehydrogenation and lost elemental nitrogen, producing a carbonized product without much weight loss. However, in the presence of oxygen, the polymer was completely burned into ashes. So we conclude that in an inert medium the PAN/CNT composite monolith was highly stable even at an extremely high temperature. In the presence of oxygen, the composite was stable below 645°C, because both MWCNT and PAN will decompose at this temperature.

In our study, we understood that the conductivity of the PAN/CNT monolith was dependent upon two main factors, such as the CNT loading and dispersion state of the CNT in the monolith. We developed composite monoliths with different CNT concentrations, ranging from 7.5 to 35wt%. The conductivity of the composite monolith with various CNT concentrations is depicted in [Figure 3](#). A gradual increase in both the electrical and thermal conductivity was observed at the CNT concentrations 7.5 to 35wt%. But when the CNT concentration increased above 25wt%, a sudden increase in conductivities occurred. We could thus develop PAN/CNT composite monoliths with electrical and thermal conductivities that were higher by more than 2.7S/cm and 0.148W/ (m. K), respectively. At low CNT concentrations, the interconnectivity between individual nanotubes was lower, because of the high porosity and

178 surface area of the PAN skeleton, which cause low conduction. The conductivities remain low
179 until the CNT interconnectivity becomes saturated in the monolith. If the concentration of the
180 CNTs within the porous body was more than the saturated value, the PAN/CNT composite
181 monolith behaved as a true conductor ([supporting information Figure S5c](#) and [Figure S5d](#)).
182 Because of a sudden bloom in the CNT interconnectivity. A rapid increase in various CNT
183 loading values are given in [Table S1 of the supporting information](#). Detailed comparative studies
184 given in [Table S2 of the supporting information](#) confirm that our CNT based PAN monolith
185 material showing outstanding properties than all other composite materials available [4].

186

187 **Figure 3.** a) Electrical conductivity values of PAN/CNT composite monoliths with various CNT
 188 concentrations (electrical conductivity of 33 wt% CNT monolith depicted in inset), and b)
 189 thermal conductivity values of PAN/CNT composite monoliths with various CNT
 190 concentrations.

In this communication we report the fabrication of advanced three dimensional porous electrical and thermal conducting PAN/CNT composite monoliths by a template-free approach. The modified thermally induced separation technique described above can be used to obtain hierarchically porous monoliths in various shapes and sizes. The porous 3D PAN/CNT composite monoliths have high CNT loading were successfully produced. The porosity, surface area, electrical conductivity, thermal conductivity and mechanical strength of the developed monolith were greater than 90%, 210m²/g, 2.7S/cm, 0.148W/(m.K) and 1.1 MPa respectively. These outstanding properties make our monolith interesting for large scale industrial applications. Our future objectives would be to carry out feasibility studies on the industrial applications of these new composites in various technological fields.

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