NANOTUBE GRAFTING IN POROUS SOLIDS FOR HIGH SURFACE DEVICES

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ABSTRACT

Natural biological systems make regular use of hair and capillary type hierarchical structures in order to create more surface area in limited space. However, very few synthetic materials are able to take advantage of this concept. This limitation can be overcome if hierarchical substrates are created by nanotube grafting on cellular materials having open interconnected porosity. The problem so far has been that growing nanotube arrays/forests on porous and microcellular surface geometries was extremely difficult. This limitation has recently been overcome by this group via pre-coating of surfaces with a plasma-derived nano-oxide layer. This process has resulted in abundant growth of carbon nanotubes (CNT) inside the pores of microcellular graphitic foams. Structure and morphology of surfaces involved, and the influence of functional oxide layer on CNT nucleation and growth have been discussed. The CNT grafted surface can have advantages in a wide variety of functional applications. For instance, it is seen that the mechanical behavior of foam-epoxy composites can be completely changed from brittle to ductile by attaching CNT on foam surfaces prior to epoxy infiltration.

Keywords: nanotube grafting, specific surface area, functional coatings, catalytic activity, microcellular foam

1   INTRODUCTION AND BACKGROUND

There is significant need for miniaturization in all modern components and devices, but most of them are currently grown on flat substrates having limited surface area. On the other hand, biological systems often adopt a so-called "hierarchical structure" by having smaller components grafted on larger substrates [1], thereby making more surface area available within limited volume. Adopting such a concept to multifunctional "smart" devices of today can be extremely beneficial in space and weight savings, as well as device efficiency, since the ultimate bottleneck in most cases is available surface area to support components.

At this time, the first generation of such a structure can be envisioned if carbon nanotubes (CNT or graphene cylinders), which are relatively well understood solids, can be grafted inside porous uneven surfaces having complex geometries. Earlier investigation in this area has been extremely limited. Investigators have often discussed nanotube reinforcement of a matrix phase that may permeate pores, but none indicate grafting of CNT on the pore walls. One study about CNT growth directly on a porous solid (silicon) indicates growth only on the outer surfaces, and not inside pores [2].

The goal of this investigation has been to investigate techniques that can enable CNT satisfactory growth and attachment of carbon nanotubes and other nanostructures on uneven surfaces having complex geometries, including three-dimensional porous solids such as foams.

2   TECHNIQUES AND EXPERIMENTAL DETAILS

Among the various techniques for fabrication of carbon nanotubes, the most common is the use of transition metals as catalyst. The most scalable one involves the use of catalytic chemical vapor deposition (CCVD) where a transition metal source (ferrocene) and a carbon source (xylene) are simultaneously introduced into the feeder gas. This has been demonstrated successfully on model surfaces such as electronic grade silicon with thermally oxidized silica[3]. It has been demonstrated that epitaxial silica, formed by controlled oxidation of silicon, can be used to pattern nanotube growth on crystalline silicon substrates. A question that arises from this, but never been addressed in the literature is whether molecular groups of silicon oxide, which is chemically similar to SiO2, but has no structural similarity with thermally oxidized silicon, can also enhance nanotube growth. This could have profound impact in creating new group of graphene-based nano-structures, since silica-like functional coatings can be applied to a wide variety of solids including porous microcellular materials[4-6]. This possibility was directly investigated in this study.

Carbon nanotubes were grown in a two stage CVD reactor with a mixture of xylene ($C_6H_4C_2H_6$) and ferrocene ($C_{10}H_{10}Fe$) injected at 235° C. The samples were kept at 800° C and subject to this deposition for specific times in a mixture of argon and hydrogen and then allowed to cool overnight in argon. Subsequently, nano-structural analysis was performed in JEOL 7401F Field Emission Scanning Electron Microscope (FE-SEM). Images were collected in backscatter, secondary emission, as well as transmission modes. Energy Dispersive Spectroscopy (EDS) data was taken for elemental analysis when needed. Surface chemical states were analyzed by X-Ray Photoelectron Spectroscopy (XPS) using a Kratos Axis Ultra System and monochromatized AlK$_\alpha$ X-rays.

Microcellular graphitic foam provided by Koopers (Figure 1) was investigated in this study for nanotube grafting.
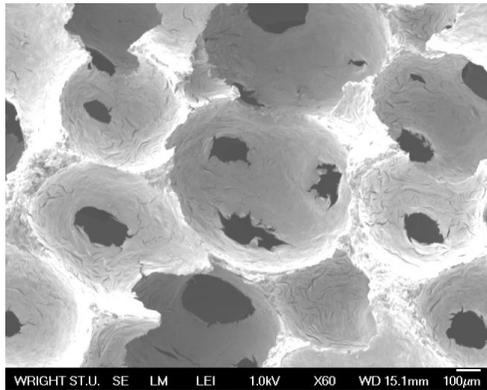

Figure 1: *Microcellular graphitic foam*

Silica treatment was done in a microwave plasma reactor, where the sample was exposed to a mixture of hexa-methyl-disiloxane (HMDSO) and oxygen in 300 W microwave power. This step resulted in a thin layer of -SiO$_2$ molecular groups attached on all open surfaces. Detailed characterization and growth mechanism of such layers have been studied extensively in this laboratory for unrelated applications, and reported in earlier publications [4-6], but the influence of such functional groups on catalytic behavior for CNT growth has not been investigated.

Untreated carbon foam was cleaned ultrasonically and functionalized with silica layer prior to CNT grafting. These were compared with uncoated foams. In addition, model studies involving surface quantifications were done on flat graphite substrates. The CCVD process was repeated on flat substrates with and without the silica coating for comparison on catalyst and CNT densities, and for detailed chemical analyses.
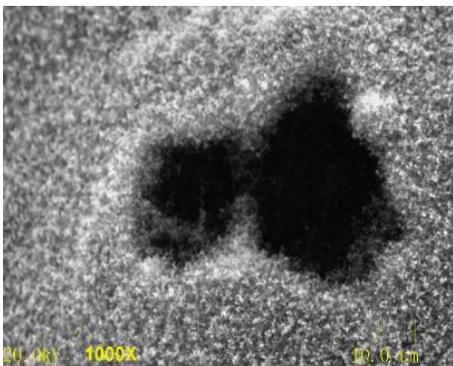

Figure 2: *CNT grafted on graphitic foam after surface functionalization with silica.*

3   RESULTS AND DISCUSSIONS

It was seen that untreated carbon foam samples showed very sparse CNT growth, whereas those treated with silica showed abundant CNT. Figure 2 shows a foam specimen covered with a dense layer of carbon nanotubes.

CNT growth can be seen inside the porous solid, through several layers of pores. Higher magnification image of the CNT growth in some pores is shown in Fig 3. It is seen that CNT diameters are in the vicinity of 10-30 nm, and nanotubes can be straight as well as coiled or helical. The extent of coiling in nanotubes can be minimized by optimizing process parameters, the most important ones being catalyst/carbon ratio in feeder gas, and hydrogen content. In general, higher ferrocene content, implying faster catalyst nucleation, results in more coiled structures. Similarly, a low hydrogen environment, resulting in faster dehydrogenation of hydrocarbons and increased concentration of atomic carbon, appears to increase the number of helical nanotubes. These indicate that coiled structure is related to rapid nucleation and/or growth resulting in higher randomness and defect probability (such as, creation of pentagon and heptagon rings of sp^2 carbon rather than proper hexagons). Some applications, especially those related to thermal or electrical properties of the hierarchical substrate may require good control of CNT helicity, since theory suggests that thermal and electrical conductivities are influenced by the helicity of nanotubes. Therefore , greater control of these structures should be investigated in future.
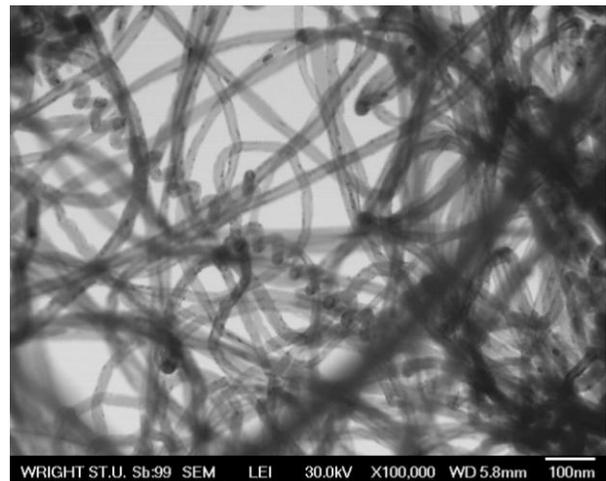

Figure 3: *Details of Carbon Nanotube morphology inside the pores.*

As far as the length of nanotubes that can be grown, there is practically no limit. Figure 4 shows that after sufficient CCVD deposition times (over 90 minutes in

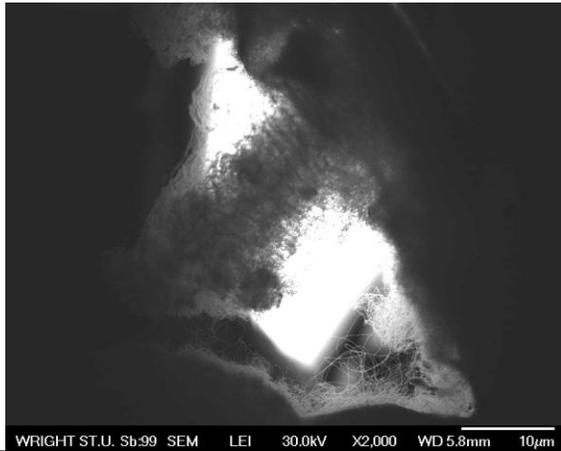this case) nanotube coils can bridge across large gaps over tens of microns.

Figure 4: *Transmission mode images show that nanotubes bundles can bridge across large pores.*

For quantitative studies, the deposition process was repeated on model flat graphite surfaces with and without silica pre-treatment. Nano-catalyst distribution on the surface was determined by backscattered image mode of FESEM during initial stages of CCVD (5 minutes), before the substrate is covered with nanotube forest. Secondary images were then taken to estimate the number of nanotubes seen to be nucleating on the same surface. The densities of catalyst particles trapped, and the average number of nanotubes nucleated per unit surface area were determined from a large number of images, and their average values noted in Table I

It is clear that the number of catalytic particles formed on the surface is increased by over an order of magnitude due to the presence of the silica layer. It is also observed that these particles are smaller, and more uniform in size and distribution. It can be seen that number of CNT fibers growing per unit area for silica-coated samples is over three orders of magnitude higher than that for untreated surfaces. If this is expressed as a fraction of catalyst particles formed initially, one can get a clear idea of the effectiveness of catalysts formed on each surface. For untreated graphitic surfaces, only about 0.1% of Fe-nanoparticles can nucleate and grow nanotubes, whereas for silica-functionalized surfaces, over 10% of Fe particles nucleate nanotube growth. This result clearly indicates that the silica functional groups not only make the surface more reactive for trapping transition metal catalysts and immobilizing them, they enhance the catalytic activity, making them almost three orders of magnitude more conducive for CNT growth. One of the reasons may be the fact that the particle sizes are kept uniformly small on these substrates.

The influence of nanotube grafting on various properties of the porous material are being investigated. This can have significance in several applications such as composite fabrication, thermal transport, electrical conductivity and biological activity. Detailed results, models and mechanisms for each type of investigation are beyond the scope of this 4-page paper. A brief discussion of the influence of nanotubes on the mechanical behavior of future composites has been provided here.

TABLE I
Average surface densities of catalyst and nanotube (CNT) [5 minute of CCVD treatment on model graphite substrate]

	Fe catalysts #/μm^2	Nanotubes #/μm^2	CNT/catalyst ratio
Untreated graphite	1×10^2	1.4×10^{-1}	0.001 %
Silica-treated graphite	1.5×10^3	1.7×10^2	12 %

Porous foam materials are often used in composites, and sandwich structures, where the structural integrity is important. To test the influence of grafted nanotubes in such structures, three slices of foam were infiltrated with epoxy to form a composite, and its stress-strain behavior tested in compression. 6 mm X 6mm samples were made from foam-epoxy composites with and without nanotube grafting. These were tested in two loading directions: normal and parallel to the sandwich interfaces. Figure 5 shows the stress-strain data for samples with each loading direction. It can be seen that in all cases, the composites made with untreated foam are brittle, and those with CNT-grafted foam show extensive plastic deformation.

This indicates that nanotube grafting can indeed change the inherent nature of the larger structures. Crack propagation and failure mechanisms of these composites have been studied in some details, and indicate that the CNTs are very strongly bonded with the carbon substrates, and CNT grafting may indeed be a very effective way of completely altering the interfacial mechanics of larger structures.

4. CONCLUDING REMARKS

In summary, biological structures often have internal and external surfaces coated with hairs, rods, fins and fibers to increase surface area and related functionality within the limited dimensions of the body. Extension of this concept to engineered devices can be expedited if one can graft smaller structures on larger supporting solids, which can be functionalized as needed. This brief paper provides insight into the possibility of creating such structures, by grafting
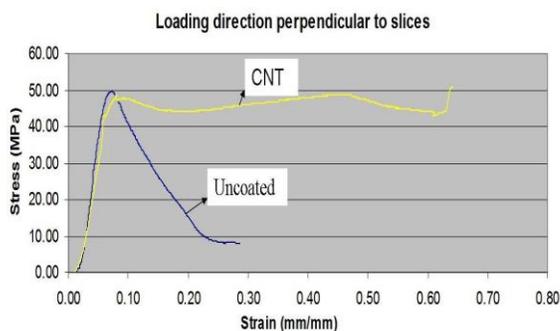
Loading direction through slices

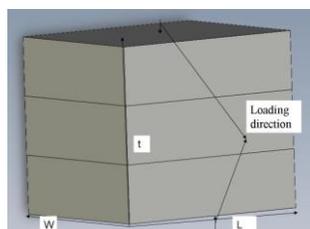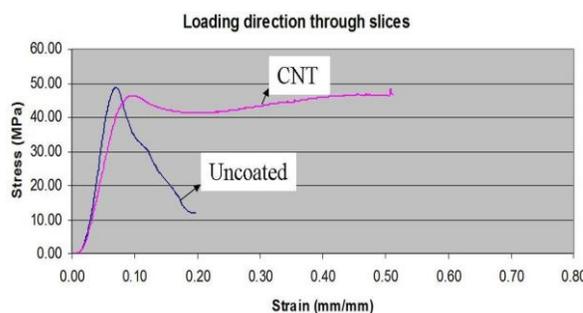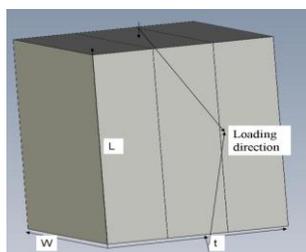**Loading direction perpendicular to slices**

Figure 5: Loading directions of composite sandwiches (left) and the stress-strain plots obtained in compression. The clear difference between the composites made from uncoated foam and CNT-grafted foam is very clear. Untreated foams fracture in completely catastrophic brittle manner, whereas the CNT grafted foams look like flattened out (plastically deformed) pieces after the test.

carbon nanotubes inside porous cellular substrates. The key to success has been initial functionalization of the porous substrate with plasma-derived silica molecules. This allows formation of smaller and more numerous nano-catalyst particles on the substrate, and also increases the probability of CNT growth per catalyst. The bond strength between nano-tubes and substrate is found to be strong. Several properties are seen to be completely altered by CNT grafting. For instance, it has been shown in this paper that the nanotubes attached to the surface of carbon foam can convert foam-epoxy composites from brittle to ductile.

5. ACKNOWLEDGEMENTS

6. REFERENCES

1. Report from National Materials Advisory Board. Hierarchical Structures in Biology as a Guide for New Materials Technology. National Academic Press: 1994.
2. Kordas, K.; Pap, A.E.; Vahakangas, J.; Uusimaki, A.; Leppavuori, S.; "Carbon nanotube synthesis on oxidized porous silicon." Appl. Surf. Sci. 2005, 252, 1471–1475
3. Wei, B.Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P.M.; "Assembly of Highly Organized Carbon Nanotube Architectures by Chemical Vapor Deposition," Chem. Mater., 2003, 15, 1598.
4. Mukhopadhyay, S.M.; Joshi, P.P.; Pulikollu, R.V.; "Thin Films for Coating Nanomaterials", Tsinghua Science and Technology, 2005, 10, 277 – 287.
5. Mukhopadhyay, S.M.; Pulikollua, R.V.; Roy, A.K.; "Surface modification of a microcellular porous solid: carbon foam", Appl. Surf. Sci., 2004, 225, 223-228.
6. Pulikollu, R.V.; Higgins, S.R.; Mukhopadhyay, S.M.; "Model nucleation and growth studies of nanoscale oxide coatings suitable for modification of microcellular and nano-structured carbon." Surf. Coat. Technol., 2008, 203, 65-72.