Autonomous Multifunctional Nanobrushes-Autonomous Materials

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ABSTRACT

In this work, taking advantage of carbon nanotubes' small size, and exceptional mechanical, chemical and electrical properties, we report on a series of nano-synthesis procedures that combine conventional chemical vapor deposition and selective substrate area growth followed by chemical functionalizations to fabricate functionalized nano-brushes from aligned carbon nanotube arrays and chemically selective functional groups. The high aspect ratio and small dimension, mechanical stability and flexibility, surface chemical and adhesive characteristics of carbon nanotubes provide opportunities to create nano-brushes with selected chemical functionalities. The nano-brushes are made from aligned multi-walled carbon nanotube bristles grafted onto long SiC fiber handles in various configurations and functionalized with various chemical functional groups. These nano-brushes can easily be manipulated physically, either manually or with the aid of motors. Here, we explain the autonomous characteristics of the functionalized nano-brushes employing functional chemical groups such that the nano-brush can potentially collect various metal particles, ions, and contaminants from liquid solutions and the air environment, autonomously. These functionalized multi-walled carbon nanotube based nano-brushes can work swiftly in both liquid and air environments. With surface modification and functionalization, the nanotube nano-brushes can potentially become a versatile nano-devices in many chemical and biological applications, where they can autonomously pick up the particles they encounter since they can be chemically programmed to function as Autonomous Chemical Nano Robots (ACNR).

Keywords: Nanobrush, multi-walled carbon nanotubes, functionalized, chemical groups, autonomous chemical nano robot.

1. INTRODUCTION

Development of modern engineering devices and structures demands inherent multifunctionalities in their constituent materials. The superior performance in physical, chemical, mechanical, structural, thermal, and electrical properties projects carbon nanotubes as an essential component of multifunctional nano- devices and structures. Many experimental and theoretical analyses thus far confirm that nanotubes are the strongest and stiffest nano-wires available with tunable electrical conductivities. Modern technological advances are capable of offering carbon nanotubes of reasonable purity and uniformity. Therefore, the time is right to develop nano integrated structures and nanoscale devices using carbon nanotubes to create *autonomous nanostructures*.

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Carbon nanotubes (CNTs) are quasi-one dimensional, nearly single crystalline (axially), hollow, graphitic carbon structures [1, 2]. The combination of high aspect ratio, small size, excellent mechanical properties [3, 4], low density, and high electrical conductivity [5] make them perfect candidates as basic building blocks for nano- devices and systems. Experimental as well as theoretical predictions [6] on nanotubes suggest axial Young's modulus of 1 TPa [7].

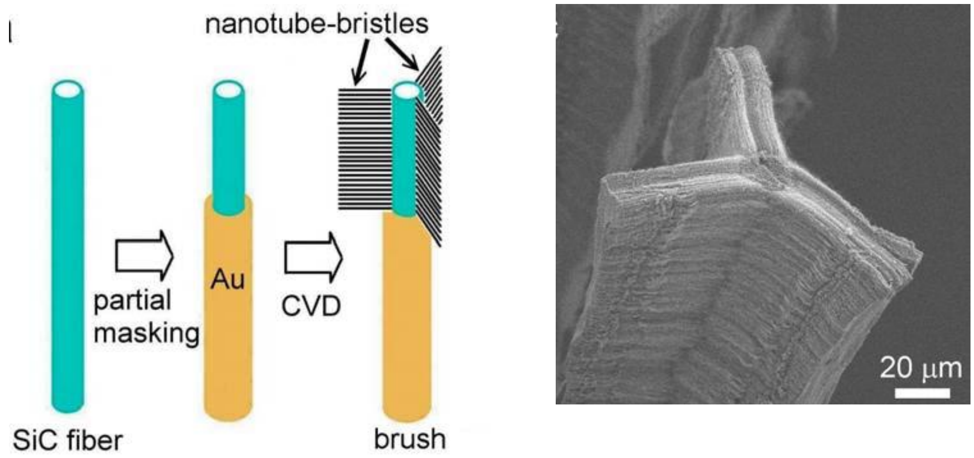
Brushes are common tools widely used in industry and everyday life. They are made into different sizes and shapes and can perform a variety of tasks such as cleaning, scraping, varnishing, painting, spreading, washing, detailing, and applying. Bristles are the most important component in a brush, which determine the applications and performance of brushes. Currently, there are mainly three types of materials used for constructing brush bristles: 1) natural products (e.g., animal hair, silk), 2) synthetic polymer fibers (i.e., Nylon, Polystyrene, Teflon, etc.), and 3) metal wires (i.e., brass, stainless steel, etc.). Each of these materials has certain disadvantages that have limited the ultimate brush performance, multi-functional usage, and life time durability. For example, metal bristles are susceptible to abrasion and degradation due to chemical exposures as well as oxidation at elevated temperature over time, and are also heavy. Natural hairs are flammable and too soft, with low mechanical strength and poor chemical resistance. Finally, synthetic fibers suffer from low thermal conductivity and stability. Carbon nanotubes seem to be ideal bristle materials, which will be strong, flexible, and are stable in chemical environments and at high temperatures (600 ºC in air). They can be bent to large angles and are able to straighten again upon load release without structural damage [8]. They have excellent thermal conductivity (>3000 W/mK), thus will dissipate heat very fast during brushing actions. They are electrically conductive, holding promise in anti-static applications. The structure of nanotube samples is inherently rough and porous, with low density (porous film is ~0.16 g/cm^3) and high surface area, allowing the fabrication of light brushes with high cleaning efficiency and functionalization capability. Most importantly, it is possible to use these nanoscale carbon nanotubes to construct brushes with much smaller size compared with conventional brushes. The motivation of making small brushes stems from the rapid development of micro- and nano-technology in recent years.

Health concerns for the increasing use and release of nanoparticles by industry have been mounting greatly recently, yet there are no effective methods/tools for the detection, cleaning, and recollection of these nanoparticles. It is therefore imperative to manufacture new-generation tools with much reduced size for targeting small area/objects, and at the same time, integrated with multifunctionality to perform a series of necessary tasks.

Here, the use of ultra-small nanoscale brushes and filters with carbon nanotubes (CNTs) as their nano-bristles are explained. Cao et al. [9] have demonstrated the direct growth of aligned multi-walled carbon nanotubes (MWCNTs) on the surface of silicon carbide (SiC) fibers for nanobrushes by chemical vapor deposition (CVD). In fact, Ghasemi-Nejhad and co-workers have demonstrated the controlled growth of MWCNTs on various substrates using the CVD technique [9-11]. Combining the CVD technique (enabling direct growth of nanotubes on fibers) and the masking method (for steering the growth area) is a simple but efficient approach to fabricate such nanotube-based nanodevices. By masking a portion of the fiber with a metal layer, the nanotubes are steered to grow only at the end of the fiber to form a brush structure with the fiber as the handle. The whole brush has an overall diameter of 20 to 100 μm [9] and can be centimeters long. Cao et al. [9] have demonstrated that the developed nanobrush possesses a range of utilities from cleaning micro-trenches of micro/nano-electronics, to painting and cleaning the inside of micro-capillary micro-tubes, to functioning as a micro/nano-switch in micro/nano-electronics and finally detecting and separating silver ions from a solution after functionalizing the nanobrush with pyrene.

2. DEVELOPMENT OF MULTIFUNCTIONAL CARBON NANOTUBE-BASED NANOBRUSHES

The general idea of creating a nanobrush structure is to mask a portion of a fiber and grow nanotubes only on one end, as illustrated in Figure 1a [9]. This simple masking technique gives precise control on the nanotube growth area and the resulting bristle span. The trim length (i.e., nanotube bristle length) can be adjusted by changing the CVD reaction time, as nanotubes grow at a relatively stable rate (~1 to 2 μm/min) over a certain period. Generally, the nanotubes grown from the cylindrical fiber surface (as the brush handle) self-assemble into three-branches symmetrically distributed around the center of the fiber (see Figures 1b). Although nanotubes initially grow uniformly from the fiber surface (see Figure 1b), they split into branches as they grow longer. Such nanobrushes can clean dusts or liquids trapped in micro-capillaries or deep holes, or when functionalized with a proper chemical functional group can detect and separate nanoparticles from a solution. [9] When the chemical functional group can adsorb more than one nanomaterial, then the nanobrush will function as an autonomous nanobrush to detect and separate the nanomaterials.



(a) (b)

Figure 1. *Nanomanufacturing of a nanobrush by growing carbon nanotube bristles at the end of a thin fiber handle [9].* ***(a**) Illustration of partial masking of SiC fibers to grow nanotubes only on the fiber top.* ***(b**) A single three-prong nanobrush consisting of nanotube bristles and a fiber handle. Bristles have a height (i.e., nanotube length) of 60 μm and span over 300 μm along the handle.*

Placing many fibers inside the furnace and on a substrate, such as silica, and spacing them 1 mm or more produces a forest of nanobrushes that can be used for large scale production.

3. SELECTIVE ADSORPTION OF PLANAR MOLECULES

A rotating brush is suitable for working in liquids, for example, the selective adsorption and removal of organic chemicals, i.e., porphyrins, functional dyes for developing photosynthetic materials [12]. This is shown schematically in Figure 2a.

In porphyrins, zinc protoporphyrin IX (ZnPP) is a planar molecule, and can adsorb strongly on nanotube surfaces through $\pi - \pi$ stacking interactions [13], whereas zinc tetraphenylporphyrin (ZnTPP) is non-planar, only weakly interacting with nanotubes. For example, Cao et al. [9] immersed a nanobrush into a solution of ZnPP dissolved in dimethylformamide (DMF) housed in a capillary and stirred for 4 min at 2,000 r.p.m. Figure 2a shows the ultraviolet−visible adsorption spectrum (Beckmann DU-4700) of the solution before and after the nanobrush stirring. The ZnPP concentration dropped from 1.5 to 0.6 mg l^{-1}, as indicated by the intensity change of the Soret band at 420 nm. Here, the porous nanotube bristles act as a 'molecule sponge' (see Figure 1d), and suck ZnPP molecules into the channels between the nanotubes. Selective adsorption was done by brushing a mixed solution of ZnPP and ZnTPP in DMF for 5 min (see Figure 2b). Although the intensity of the Soret band (at 425 nm) gradually decreased from 1.1 to 0.7, a shoulder at 403 nm clearly emerged, which is a characteristic peak of ZnTPP, indicating that ZnPP had been selectively removed (the concentration of ZnTPP remained unchanged, whereas the relative concentration ratio of ZnPP/ZnTPP decreased from 2.7:1 to 1.1:1). After rotation in solution, the nanobrushes retained their structure and no nanotubes shed and contaminated the solution [9].

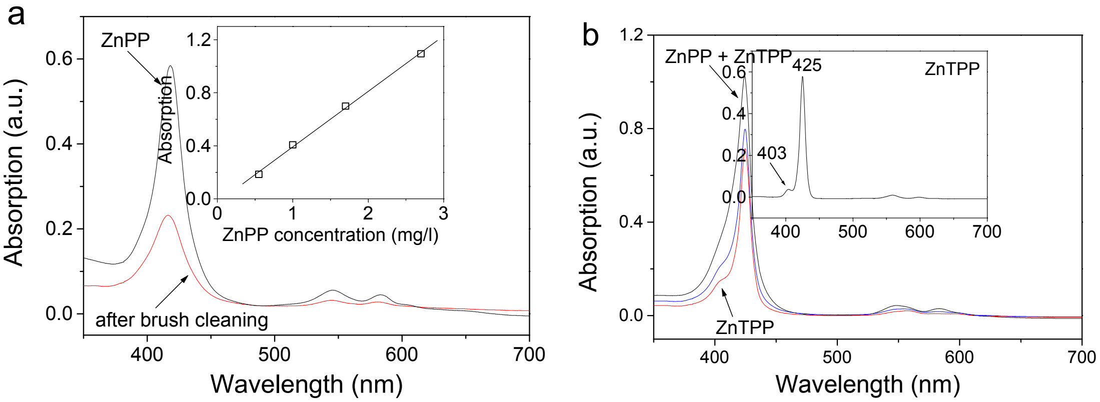


*Figure 2. Selective adsorption of chemicals from solution by nanobrushes [9]. (**a**) UV-Visible spectrum of ZnPP solution (in DMF) before and after rotate-brushing. The peak at 420 nm is the Soret band of ZnPP. Inset: Characterized ZnPP concentration versus Soret band intensity. (**b**) Selective adsorption of ZnPP from a mixture of ZnPP (1.35 mg/l) and ZnTPP (0.5 mg/l) after brushing the solution for different times (middle curve: 2 minutes; lower curve: 5 minutes). The emergence of a shoulder (403 nm) nearby the Soret band (424 nm) indicated that more ZnTPP was left in the solution while ZnPP had been selectively adsorbed. Inset: UV-Visible adsorption spectrum of pure ZnTPP with a characteristic peak at 403 nm (see arrow).*

4. REMOVAL OF HEAVY METAL IONS

One of the most intriguing properties of carbon nantoubes is their ability to be functionalized by chemical groups to target specific species. There have been many reports about the functionalization of nanotubes with appropriate groups, and making nanotube sensors for chemicals, proteins, glucose, and enzymes [14]. For example, DNA strands could be attached to the nanotube surface, and then this grafted nanotube would attract another DNA strand with complementary structure. Cao et al. [9] have also demonstrated the grafting of nanotube nanobrushes with 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt groups (with negative charges on the sulfonate groups), enabling the CNT nanobrushes to pick up silver ions (Ag^+) from a silver nitrate solution (see Figure 3). XPS (X-ray Photoelectron Spectroscopy, Perkin Elmer XPS 5500) analysis showed that the pyrene-functionalized nanobrushes could effectively adsorb Ag(I) ions, while the as-grown (i.e., non-functionalized) nanobrushes had no capacity for the adsorption of Ag(I). This leads to the potential application of nanobrushes in removing heavy metal contaminants from water and other solutions. Therefore, the functionalized nanobrushes (see Figure 3) can remove dissolved species such as heavy metal ions (for example, Ag^+) in a solution (for example, silver nitrate, lethal to fish in concentrations of 0.076 g ml^{-1}). The ionic pyrene derivative (1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt) with three sulfonates per molecule was grafted onto the nanotube nanobrushes to pick up Ag^+ by the electrostatic attraction between the negatively charged sulfonate function and Ag^+ through a simple 'dip' action (see Figure 3, left) [9]. The nanobrushes were soaked into 20 ml silver nitrate ($AgNO_3$, 0.1 N) for 10 minutes, which was kept stirred, and then rinsed in distilled water to remove the residue solution on the nanobrush surface. As-grown nanobrushes without any functionalization were tested for reference. The adsorption of silver on the nanobrushes was characterized by X-ray photoelectron spectroscopy (XPS) (Perkin Elmer XPS 5500) [9]. The pyrene-nanobrushes showed two clear peaks (Ag 3*d*) at a binding energy of around 370 eV, whereas as-grown nanobrushes did not show observable Ag adsorption (see Figure 3, right). Calculation based on the peak (intensity) area of Ag relative to C (done by the RBD AugerScan Software upgrade) showed an Ag percentage of 0.1% (number of atoms). Small particles and aggregates were observed on the nanobrush surface after H_2 reduction, confirming the adsorption of silver ions [9]. In the work performed by Cao et al. [9], they relied on the electrostatic attraction of the positively charged Ag(I) ions to the negatively charged sulfonate groups on the pyrene. However, such an interaction is not likely to be specific for Ag(I). By appending the appropriate small organic molecules to the nanobrushes, some specificity for the interactions with metal ions in solutions can be demonstrated by the use of proper chemical functional group(s) that have the ability to adsorb a variety of ions from a solution. This will make the nanobrush an *autonomous adaptive nanobrush* to detect and separate a variety of ions. For example, the nanotube nanobrushes can be covalently functionalized, using defect group chemistry, where the carboxy groups can be converted to the corresponding ω-thiomethyl amides following activation with thionyl chloride and exposure to an excess of the thiomethyl amine. The length of the alkyl tether can be varied. For example, the nanobrushes prepared from these functionalized nanotubes can separate Ag(I), Au(I), Hg(II), Cd(II), and Pb(II) ions from aqueous media. Non-covalent functionalization of the nanotubes can also be performed. 9-Anthracenylcarboxylic acid can be converted to the same series of ω-thiomethyl amides, and used to functionalize the nanotube surface.

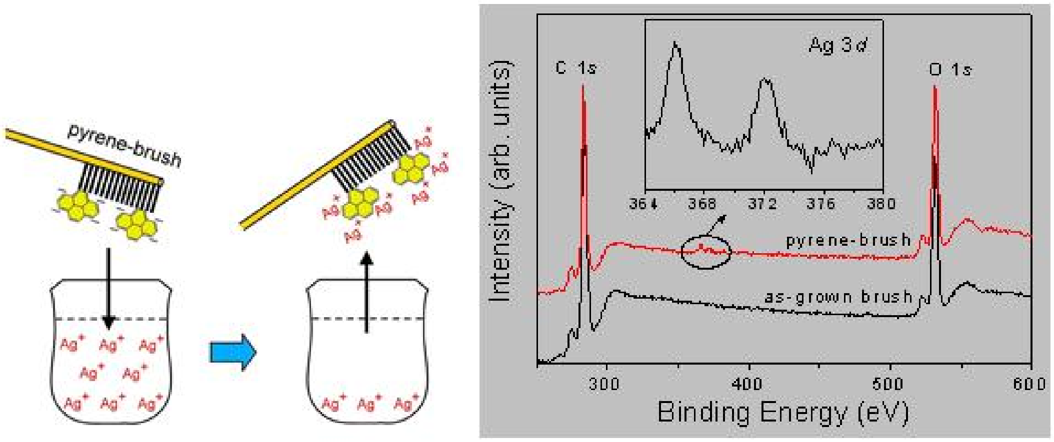


Figure 3. ***(left)*** *Schematic showing the Pyrene-functionalized nanobrushes and using them to pick up silver ions from* $AgNO_3$ *solution.* ***(right)*** *XPS spectrum of Ag adsorption by as-grown (black) and pyrene-functionalized (red) nanobrushes. Inset: Ag 3d peaks from pyrene-nanobrushes [9].*

5. CARBON NANOTUBE-BASED AUTONOMOUS NANOFILTERS

The general approach of creating an autonomous nanofilter structure is to mask the outer surface of a quartz tube and grow nanotubes only on its inner surface, as illustrated in Figures 4 and 5, schematically. The trim length (i.e., nanotube length) can be adjusted by changing the CVD reaction time, as nanotubes grow at a relatively stable rate (~1 to 2 μm/min) over certain period. Generally, the nanotubes grown from the inner surface of the cylindrical tube self-assemble axisymmetrically and are uniformly distributed about the center-line of the tube and grow radially, resulting in a filter-type structure (see Figures 4 and 5). The CNTs of these nanofilters can be functionalized by proper chemical functional group(s) to detect and separate chemicals and metal ions or nanoparticles from a solution. When the chemical functional group can adsorb more than one nanomaterial, then the nanofilters will function as *autonomous nanofilters*.

Figures 4 and 5 show two types of nanofilters for various filtering stages. For example, the Stage-I (see Figure 4) type nanofilters can be used for the initial stage of filtering, and Stage-II (see Figure 5) type nanofilters can be used for the final stage of filtering. Obviously, in practice, a series of filters can be assembled from Stage-I type filter to Stage-II type filter, starting with a larger hole at the center-line of the Stage-I and gradually decreasing the diameter of the hole in the subsequent filters ending with Stage-II type filters. The nanofilters CNT functionalization follow similar procedures as explained for the nanobrushes.

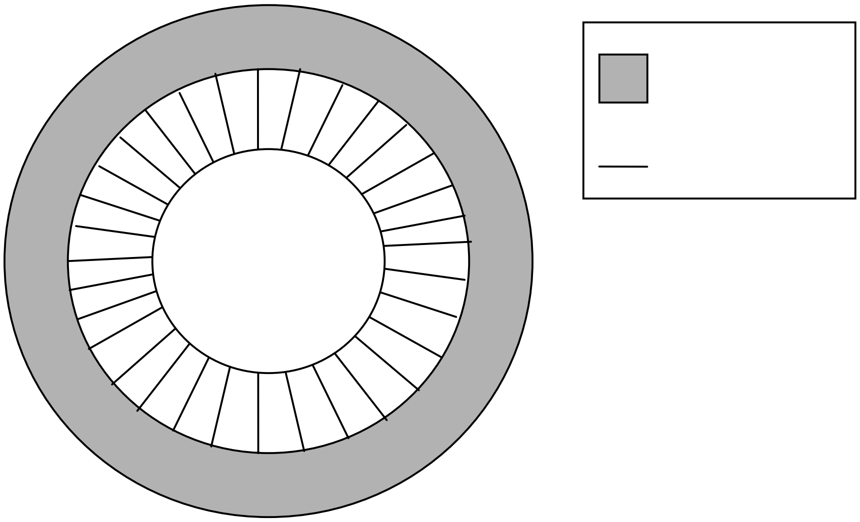


Figure 4. *Stage-I Autonomous Nanofilter: Nanomanufacturing of a nanofilter can be performed by masking the outer surface of a quartz tube and growing carbon nanotube on its inner surface leaving a fluid passage hole at its center.*

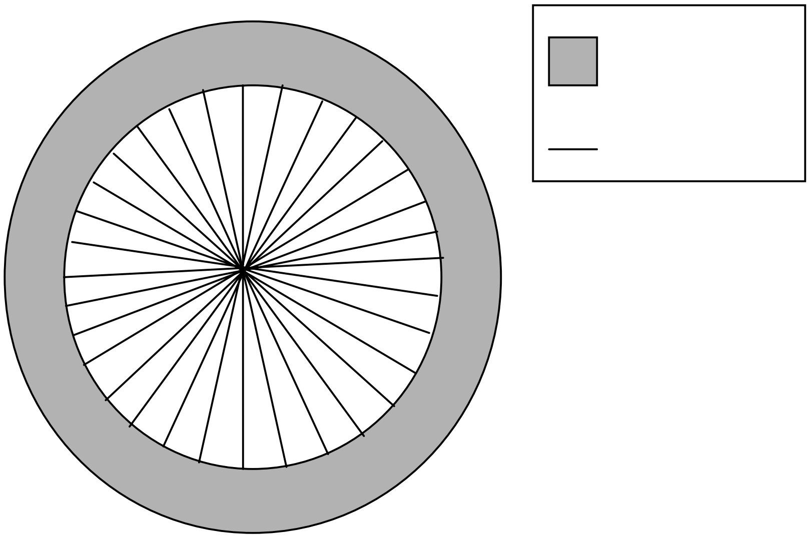


Figure 5. *Stage-II Autonomous Nanofilter: Nanomanufacturing of a nanofilter can be performed by masking outer surface of a quartz tube and growing carbon nanotube on its inner surface to fill the entire hole of the quartz tube.*

6. CONCLUSIONS

Autonomous nanobrushes and nanofilters are introduced. The basic components of these autonomous nanodevices are mutlti-walled carbon nanotubes that due to their geometry, size, and physical and chemical properties allow for chemical functionalizations, such that the functionalized nanotubes within the nanobrushes and nanofilters are capable of separating metallic ions from solutions with applications in environmental cleaning. The carbon nanotubes within the nanobrushes and nanofilters can be functionalized with appropriate chemical functional group(s) such that the functionalized nanotube can separate a variety of metallic ions, rendering the nanobrushes and nanofilters *autonomous nanodevices*, where these nanodevices can separate a variety of ions without a prior knowledge of the "pollution elements" within the solutions.

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