Nomination Package for the '2012 Presidential Green Chemistry Challenge Award'

Upcycling Waste Plastic Bags into Valuable Carbon Nanotubes and Carbon Spheres

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Recent milestone: In between Jan. 2008 and Dec. 2011, Argonne National Laboratory chemist Dr. Vilas Pol researched, demonstrated, implemented, and patented an environmentally friendly upcycling process for the remediation of ubiquitous waste plastic bags into highly valuable carbon nanotubes and spheres. This significant upcycling discovery resulted into 4 patent applications, 3 articles in an environmentally motivated research journals and quotation in numerours international media outlets. The efforts on pilot plant construction and commercialization of the processe are underway.

Eligible Organization: The nominated technology is eligible under nonprofit organizations.

Focus area 2: The use of greener reaction conditions

U.S. Activities: The technology was developed and tested entirely in the U.S. at Argonne National Laboratory, IL and will be commercialized in the USA based on filed 4 US patents.

Abstract: Every year, the global economy discards 34 million tons of plastic wastes, most of it becomes a liability, clogging landfills and oceans, or entering the atmosphere through incineration. Argonne's original, innovative upcycling process converts these ubiquitous waste plastic bags (WPB) into valuable carbon nanotubes (CNTs) and carbon spheres (CSs), which exhibits remarkable mechanical, adsorption and electrical properties. Upcycling process offsets the extraction of raw materials from the environment and removes plastic from landfills that would otherwise degrade an aerobically to methane, a potent greenhouse gas. It also reduces air and water pollution, ultimately lessening the hazards to public health and the environment.

Argonne's solid-state, controlled pyrolysis process involves heating of individual or *mixed* WPB in a sealed chamber to 700°C, where carbon and hydrogen atoms separate to form carbon structures and hydrogen gas. Conventional production of CNTs requires inputs of hydrogen and ethylene gases derived from fossil fuels, whereas upcycling process consumes WPB. Our recent *advancement* is exceptionally successful on the utilization of alternative iron based inexpensive and friendly catalyst (ferrocene), avoiding the use of toxic cobalt acetate catalyst. With no catalyst, the upcycling process yields smooth, micrometer-sized, amorphous CSs that are conductive, hard and paramagnetic *(Publication 1)*. This developed process is solvent-less, requires low-energy and is low-emissions. The obtained carbon products are highly valued throughout the clean energy industry in applications including fiber-glass for wind turbines, lightweight carbon composites for transportation, electronics, as additives for lubrication and electrode materials *(Publication 2)* for batteries and super capacitors.

Taking advantages of Argonne's existing inventions, prototype reactor and accessible knowledge on optimization of reaction conditions, a team of Northwestern University, IL graduates are scaling up this technology and conducting market survey (Bagpipe Technologies) at Farley Center for Entrepreneurship and Innovation. With the great licencing interest Grupo Simplex and G2 NanoTechnologies, LLC are working with Argonne to commercialize this technology. Industrial collaborators, Superior Graphite and ConocoPhillips heat-treated CSs at higher temperatures; which improved the electrochemical performance as an anodes of lithium-ion batteries. Argonne's tribology department utilised upcycled CSs and CNTs as an additives of lubricating oils, minimizing friction and wear *(Patent application 4).*

Background: The Problem with Plastic

Plastic bags are strong, lightweight, convenient and cheap, making them highly *attractive* for businesses and consumers. According to a 2007 survey by the Environmental Protection Agency, only 13% of the over 100 billion plastic bags that Americans use every year are recycled [1]. The rest pile up in landfills, litter roadsides, and block drains. They are energetically expensive to make: Given that a single grocery bag requires approximately 0.48 mega joules of energy to be produced (the equivalent of the amount of energy consumed by the average passenger car traveling 1/8 of a kilometer), the production of 100 billion plastic grocery bags equals 7.75 billion miles of automobile travel, which at 30 miles per gallon average efficiency, equals 258 million gallons of **gasoline**. Apart from gasoline input; the disposal of used plastic bags is a worst problem. Since plastics are not biodegradable, storing them in landfills is not an effective solution; incinerating them is expensive and can release **toxic** gases. Moreover, chemically different WPB does not yield homogenous products via extrusion, making cost ineffective and challanging to the current recycling facilities. Therefore, the waste plastic bags remained huge environmental burden on our society with limited conventional recycling abilities.

Carbon products and potential market size

The carbon black (commonly referred as 'soot') [2] with irregular morphologies are produced by the incomplete combustion of heavy petroleum products such as coal tar, ethylene cracking tar, and vegetable oils. Industrial carbon blacks are used in a wide variety of applications, including printing inks, toners, coatings, plastics, paper, tires and building products with their exceptional pigmentary, electrical, UV absorption, and rheological properties. Currently, worldwide carbon black consumption is 9 million tons per annum, expected to reach 13 million tons by 2015 [3].

Moreover, CNTs are the fastest growing segment in nanomaterial technology market across the globe. By virtue of CNTs' curved graphitic structure, smaller diameter, and high aspect ratio, they possess many appealing properties and *potential* applications that include mechanical actuators, electronics, catalysis, sensors, high-strength composites, and adsorbents [4]. The global CNTs market is estimated to reach $700 million by 2012, while production capacity is estimated to grow from 5 metric tons in 2012 to 14 metric tons in 2016 (30.6% Compound annual growth rate, CAGR). Currently, there are over 300 CNTs producers in the world, offering a variety of CNTs at various dimensions and properties. Most of these players are located in China, producing industrial scale CNTs through fluidized bed Chemical Vapor Deposition (CVD). The Asia-Pacific market is driving the CNTs sales and is expected to hold 49% of the global demand, followed by the United States and Europe. The European CNTs market is the fastest growing region with an estimated 50% CAGR, with Germany drawing 43% of the European CNT demand [5].

Upcycling vs. existing processes

To address an important global environmental issue, a solvent-less, inexpensive process to degrade WPB or their mixtures in a controlled way has been developed at Argonne. The process involves thermal decomposition of WPB at or below 700 ^{o}C in a specially designed reactor (Figure 1a) under an inert or air atmosphere. The solid WPB, upon heating in a close atmosphere, converts to its critical phase. The natural cooling of the critical phase yields micrometer sized (2 to 10 µm diameter), spherical CSs with smooth surfaces (Figures 1b). Produced dry high purity (>99% of C) CSs do not need further chemical processing, which is a great advantage. The Raman spectrum of the CSs is a characteristic of a mixture of disordered, D (1330 cm^{-1}), and nanosized graphitic, G (1590 cm^{-1}) carbon. The XRD pattern of the CSs depicts a high relative intensity ratio of the 002 to 110 main diffraction peaks of the graphitic lattice, with calculated interlayer spacing of 0.34 nm. The measured Brunauer-Emmett-Teller (BET) surface area of CSs is ~ 3 m^{2}/g and the true density of 2.1 g/cc *(Publication 2)*. Such CSs are not available in current market, making themselves inimitable and significantly valuable for myriad novel applications.

Furthermore, with the addition of cobalt acetate (~20 wt%) catalyst during the thermolysis of low density polyethylene (80 wt%), ~ 1000 PSI pressure autogenically created, under which several microns long with less than 80nm CNTs are yielded *(Publication 3)*. The reaction time varies from one minute to 3 hrs depending upon CNTs growth requirements. Our recent *advancement* is highly successful on the utilization of an alternative ferrocene catalyst, growing >90% CNTs (Figure 1c), avoiding the use of toxic cobalt based toxic catalyst. Though the trapped Fe catalyst (<10%) can be removed via acid treatments, we try to use CNTs as produced for assorted applications, reducing the cost of chemical processing.

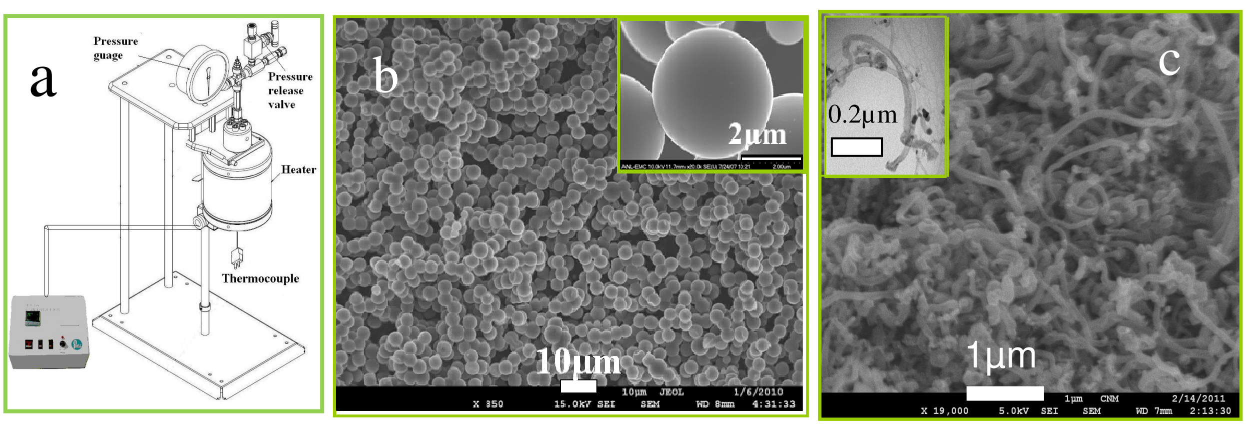


Figure 1. WPB upcycling reactor (capacity = 80 cm^{3}), b) Scanning electron micrographs (SEM) of carbon spheres obtained from WPB, and c) SEM of CNTs by upcycling the mixture of low density polyethylene bags with ferrocene catalyst (inset shows transmission electron micrograph)

At present, CNTs can be made by laser ablation, fluidized bed reactors, electric arc discharge and chemical/plasma vapor deposition methods. Beside the catalysts, these methods generally require a petrochemical feedstock, vacuum environment and special ambient gases (e.g. ammonia, nitrogen or hydrogen) to prevent carbon from high temperature oxidation. Beyond that these techniques produce CNTs in relatively small-scale batches, leading to high production cost. Generally, a huge heat input is needed in the carbon production by all existing technologies;

however upcycling technology needs *less energy* input since it operates under the self-generated pressure during substituted WPB feedstock thermolysis. The contaminated plastic bags with oil or other hydrocarbons will not have any negative impact on the CSs or CNTs production. However, it will be advisable to avoid heavy metals ingress as they are likely to become hazardous contaminants in the carbon products. Although micron size solid CSs are non-toxic, CNTs may exhibit pulmonary toxicity. Therefore, to prevent inhalation of CNTs, preparation and handling are/will be carried out by following the established methods of industrial hygiene to keep CNTs work environmentally safe for workers. EPA will be notified 90 days prior to the mass production of CNTs via upcycling.

Argonne's upcycling process is the most straightforward (no need of petroleum precursors, vacuum or ambient gases) and a unique way of WPB remediation. The price of multiwalled CNTs vary with tube diameter, lengths and impurities. Current competitive cost of CNTs is around $5-$10/gram for 60-100 nm outer diameters. On a commercial basis, Argonne's finicky 'upcycling' process should be able to reduce this cost significantly (minimum by 5 times), due to the simplicity of production via clearing problematic pervasive WPB.

Applications of upcycled carbon nanotubes and carbon spheres

1) *Electrode materials for rechargeable lithium ion batteries:* The CSs obtained from used numerous WPB are tested as an anode material for lithium ion batteries. The heat treated CSs *(by superior graphite)* produced 250mAh/g reversible specific capacity for hundreds of cycles (Figure 2a) with > 99% columbic efficiency *(Patent applications 1).* The unique spherical shape of carbon anode particles offers the possibility of smoothing the current distribution at the carbon electrode surface during charge - thereby reducing the risk of lithium dendrite formation, leading to the fabrication of safer battery electrodes. The maximum achieved specific capacity from the upcycled cobalt encapsulated in CNTs *(Patent applications 2)* is ~ 372mAh/g after 200 cycles (Figure 2b), when cycled at 1C rate in between 5mV and 3V, equivalent to the theoretical capacity of graphite [4]. Not only are cobalt or iron (catalyst) encapsulated CNTs good candidates as an anode for Li-ion batteries, they also are *excellent* entrant as a cathode of metal air batteries *(Patent application 3).*
2) *Additives for lubrication:* The friction and wear studies of as-prepared dry CSs and CNTs after mixing with lubricating oils are successfully performed at Argonne's Tribology department. Figure 2c, left panels confirms the relatively *low friction behavior* of novel carbon-based colloidal oil compared to conventional oil at different speeds. Figure 2c, right panels illustrate the occurrence of *low wear* (high wear-resistance) for novel carbon based colloidal oil due to formation of dark chemical carbon film *(Patent application 4)* on the rubbing surface, whereas there was absence of chemical film on the conventional oil that resulted in high wear and friction.
3) *Water purification:* A simple, straightforward laboratory test confirmed the hypothesis that upcycled CSs and CNTs are useful in water purification due to their adsorption properties *(Publication 3).*
4) *Other applications:* The electrical conductivity of an individual CS was measured employing sophisticated scanning tunneling microscopy (STM). Two electrodes were attached to single CS, which recorded minimum resistance of R= 440 Ω (Figure 2d), reproducibly. Considering the area and length between the two probes attached to a single CS, the electrical conductivity

of 45 S/m is calculated *(Publication 2)*. Due to their conducting nature, the CSs can act as virtuous candidates for black paints as well as heat dissipating carbon bodies (20 wt% in rubber) for tire industries. Additionally, CSs became fascinating candidates for printer ink and toners due to their required micrometer size diameters with the addition of suitable additives. To measure tensile strength of an individual CS, nano-indentation measurement is carried out. A single CS mounted on a diamond substrate was subjected to an applied force (2.5 N) using a diamond indenter and the load-displacement curves (Figure 2e) are measured. Remarkably, we found that both the CS and the diamond substrate exhibit similar hysteresis curves analogous to indenting on diamond substrate. This implies that the hardness and Young's modulus of CSs are close to those of diamond [1000 GPa], which is a result of mixture of sp^2/sp^3 nature of carbon sheets and their layer-by-layer assembly under the autogenic (400-1000 PSI) pressure.

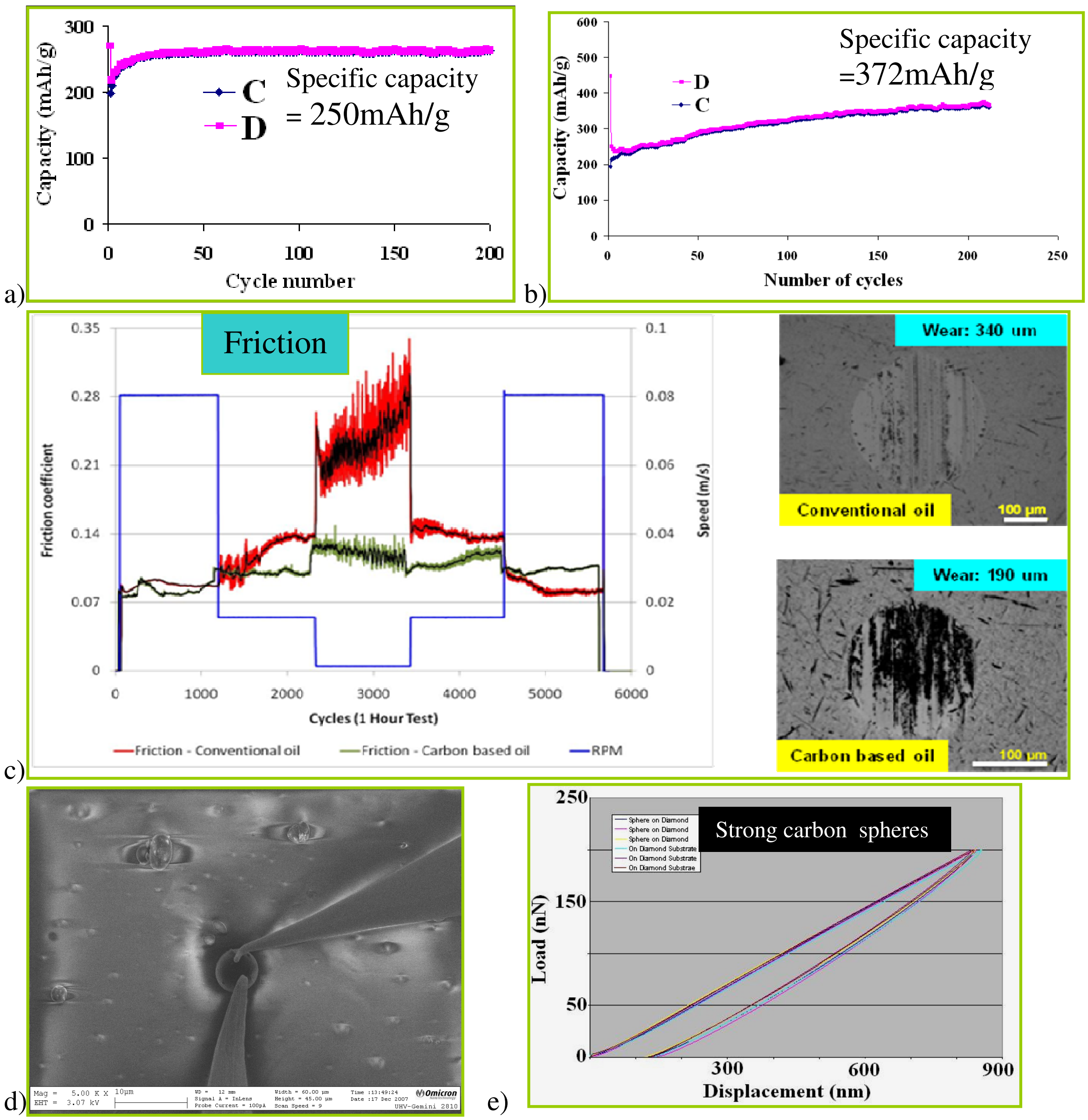


Figure 2. Long cycle discharge-charge performance of a) heated CSs, b) CNTs at 1 C rate, c) Comparison of friction (left) and wear (right) test results, d) electrical conductivity measurement of single CS, and e) Load vs. displacement curves on single CS.

US Patent applications

1) V. G. Pol and P. Thiyagarajan, A process for remediation of plastic waste, US 2010/0178232
2) V. G. Pol, S. V. Pol, M. M. Thackeray, Autogenic reactor for battery materials manufacture, US 2011/0104553
3) C. S. Johnson, V. G. Pol, Z. Zhang, Lithium-Oxygen electrochemical cells and batteries, US 2011/0104,576
4) V. G. Pol, M. M. Thackeray, K. K. Mistry, A. Erdemir, Novel carbon materials as additives for advanced lubrication, ANL-IN-10-021

Related publications

1) V. G. Pol, Upcycling: Converting waste plastics into paramagnetic, conducting, solid, pure carbon microspheres, ***Environ. Sci. & Tech.*** 2010, *44* (12), 4753.
2) V. G. Pol, M. M. Thackeray, Spherical carbon particles and carbon nanotubes prepared by autogenic reactions: Evaluation as anodes in lithium electrochemical cells, ***Energy & Environmental Science,*** 2011, 4, 1904–1912 *(with front cover).*
3) V. G. Pol, P. Thiyagarajan, Remediating plastic waste into carbon nanotubes, ***J. Environ. Monitoring,*** 2010, 2010, *12*, 455 (Honored as a *'Top 10 papers'* in Feb. 2010).

There are very few examples where a cheap commodity material can be recycled into a high value application. Above all significant findings overcome one of the foremost deficiencies of the recovery and recycle of commodity materials – positive economics through value creation.

Media Recognition to upcycling technology

- To celebrate, *International Year of Chemistry* (IYC 2011), ChemistryViews Wiley, Weinheim, Germany organized an international video competition themed 'Chemistry in everyday life', where international spectators and judges voted to upcycling technology video and awarded '*Second Prize*'. http://www.chemistryviews.org/details/news/969835/ChemistryViews_Video_Contest.html
- *Dr. Bill Brinkman,* Office of Science Director and Dr. Vilas Pol of Argonne are discussing the upcycling technology on the occasion of Earth Day celebration (April 21st, 2011, Washington, DC) http://science.energy.gov/news/in-focus/2011/04-22-11-2/
- On the occasion of 'Earth Day 2010', American Chemical Society's '*Environmental Science & Technology*' journal organized a worldwide video competition aimed on 'How Chemistry Helps YOU Be Green?' Argonne's submitted video entry 'Plastic Bags to Batteries: A Green Chemistry Solution', http://www.youtube.com/watch?v=q17Bd6tOMHI won a '*Grand Prize*'.

With the substantial societal interests, international media outlets; *PBS NOVA*, ABC7, Univision, Asia TV, Jeopardy, Discovery, New Scientist, RSC, ACS highlighted this greener technology.

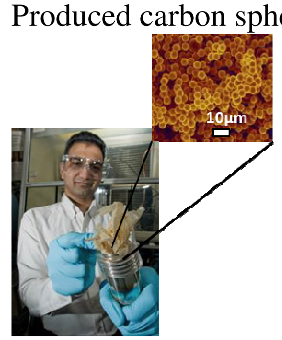
▸ NOVA, PBS (David Pogue) Making Stuff: Cleaner, February 2, 2011 (8.00 pm, CST) http://www.youtube.com/watch?v=jiC4j3C_0D4

- ABC 7 TV, Chicago, From the landfill to lithium-ion batteries, Jan. 15, 2010 (5:00 pm) http://abclocal.go.com/wls/story?section=resources/lifestyle_community/green&id=7221431
- New Scientists (Helen Knight) Green machine: Tackling the plastic menace, June 28, 2010 http://www.newscientist.com/article/dn19097-green-machine-tackling-the-plastic-menace.html Geoffrey Mitchell of the University of Reading in the U.K., says the fact that the Pol's process uses no catalyst is a major plus, and if the technique can be used to recycle the growing mountain of low-value, mixed plastic waste, it could have *"a rosy future"*.
- Discovery News (By Jessica Marshall): Plastic bags into power? June 25, 2010 http://news.discovery.com/earth/plastic-bags-power-recycling.html Nishkamraj Deshpande of the United Space Alliance (NASA contractor) commented that "Microspheres are expensive to make using the current technology"—which makes Pol's new method *appealing*.
- ACS's Chemical Sciences and Engineering news "Turning Plastic Trash into Treasure? May 28, 2010 http://pubs.acs.org/cen/news/88/i22/8822news6.html

Presented solvent-less upcycling process allows continued use of business and user-friendly plastic bags via remediating them into industrially significant value-added carbonaceous products. The production cost of distinctive CSs and CNTs would be significantly lower than the existing technologies due to lower cost of raw materials and processing. The invention is reduced-to-practice, and a wide range of applications in energy devices, lubricants, harder/light weight tools, filtration, the aerospace industry, toners, paints, and tires as reinforcement of rubbers are anticipated. The demonstrated green 'upcycling' process resolves one of the major problems faced by today's modern society, avoiding plastic waste entering into landfills. Based on provided evidences, Argonne strongly believes that this nominated green technology meets the scope of the program and is highly suitable for the '2012 Presidential Green Chemistry Challenge Award'.

Besides the development of upcycling process, the primary inventor of this technology is a scientist of prodigious caliber, published 90 peer-reviewed articles, 4 book chapters and achieved 1,700 citations ('h index' 22). He was invited to deliver talks in numerous conferences including 2011 Plastic recycling conference, New Orleans. He is an editorial board member of 5 international journals including 'Green and Sustainable Chemistry', Scientific Research Publishing, USA. He won many awards including Intel Prize, Science as Art, Grand Prize, Director's postdoctoral fellowships at Argonne and Los Alamos National Laboratory's as well as silver & gold medals.

Produced carbon spheres



'Upcyling' of waste plastic bags

References

1) Salmiaton, A. et al. *Waste Management,* **2007,** 27, 1891;
2) Inagaki, M. *Carbon,* **1997**, *35*, 711;
3) http://www.intertechpira.com/The-Future-of-Carbon-Black-to-2015.aspx
4) Smalley, R.E. et al. *Science,* **1996,** *273***,** 484;
5) http://www.prweb.com/releases/carbon_nanotubes/nanotechnology/prweb4482634.htm