



# ChemFiles

## Nanomaterials for Advanced Applications

Vol. 5 No. 3

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## Nanomaterials Yesterday, Today and Tomorrow

Mr. Thomas Juehne, Sigma-Aldrich Corp., St. Louis, MO USA

The union of distinct scientific disciplines is revealing the leading edge of Nanotechnology. Fifteen to twenty years ago, the interdisciplinary activity of geneticists, biologists, immunologists and organic chemists created a more diverse toolbox now known as life science. Bioconjugates were created to help us move from outside the cell to the inside. Enabling technologies brought about the ability to create, identify and specifically manipulate genetic maps to engineer designer proteins.<sup>1</sup> In parallel, physicists, chemists, polymer chemists and engineers were creating the foundation for the small world of nano materials science. Fullerenes,<sup>2</sup> carbon nanotubes<sup>3</sup> and atomic force microscopy<sup>4</sup> were in their infancy. In less than a decade, materials science and life science together are unraveling the mysteries of controlling, on a molecular level, the structure of matter.

Particles, complexes, tubes, coatings, active surfaces and devices are being explored on the nanoscale. Assembly of nature's building blocks (e.g. carbon, nucleic acids, lipids and peptides) along with the combination of different materials (e.g. CdSe/ZnS, Au, Ag, Si(n)OH(n), light harvesting dendrimers and thin films) are leading to insightful understanding and the creation of new scientific tools. Chemists and physicists have been manipulating matter on the molecular level for centuries. Some say this is nothing new. When one looks at the absolute elegance of the nanometer scale biological system, however, one is compelled to create, understand, manipulate and control systems with equal elegance.

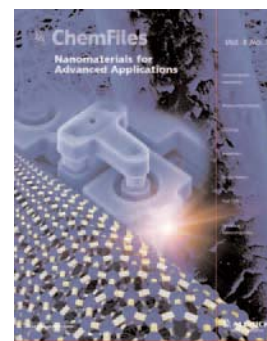
This high level of activity and promise has attracted private and government funding with considerable economic impact and growth. Since the launch of the American National Nanotechnology Initiative ([www.nano.gov](http://www.nano.gov)) in 2000, there have been hundreds of start-up companies emerging in the market. At universities, there are increased investments in nanotechnology programs and facilities. Northwestern University's Institute for Nanotechnology ([www.nanotechnology.northwestern.edu](http://www.nanotechnology.northwestern.edu)) is a direct result of the high level of activity and pioneering work of Prof. Chad Mirkin. As a result of massive grant support and continued focus from the university, the Center for Nanofabrication and Molecular Self Assembly building has been constructed. Similarly, The Molecular Foundry ([www.foundry.lbl.gov](http://www.foundry.lbl.gov)), a Department of Energy Nanoscale Science Research Center, is under construction at Berkeley in California. The research center is focused on the dissemination of nanoscale techniques and methods to enable scientists to delve into nano research. The Molecular Foundry is the direct result of Prof. Paul Alivisatos' discoveries and benchmark work. We see an increase in programs, facilities, career opportunities and educational outreach. It is a massive explosion of activity in study on a very small scale. Science is beginning to set free nanotechnology. Soon the only limit will be the imagination.

### Acknowledgements

Sigma-Aldrich would like to gratefully acknowledge the contributors to this applications guide, especially Prof. William E. Buhro, Dr. Sean Dingman, Mr. Thomas Juehne, Prof. Nicholas A. Kotov, Prof. Yuri Lvov, Prof. Shelley D. Minteer, Prof. Pradeep K. Rohatgi and Prof. Michael Strano.

### About the Cover

The cover image depicts part of a MEMS actuator (image courtesy of MEMSX, <http://www.memx.com/products.htm>) in the foreground as well as a molecular model of a single-walled carbon nanotube (image courtesy of Prof. Chris Ewels). The background image shows a tight-knit mesh of nanofibrils with a human hair overlaid for a size comparison (image courtesy of Espin Technologies, Inc.).



## Nanoparticle-Catalyzed Growth of Semiconductor Nanowires

Prof. William E. Buhro, Department of Chemistry, Washington University, St. Louis, MO USA

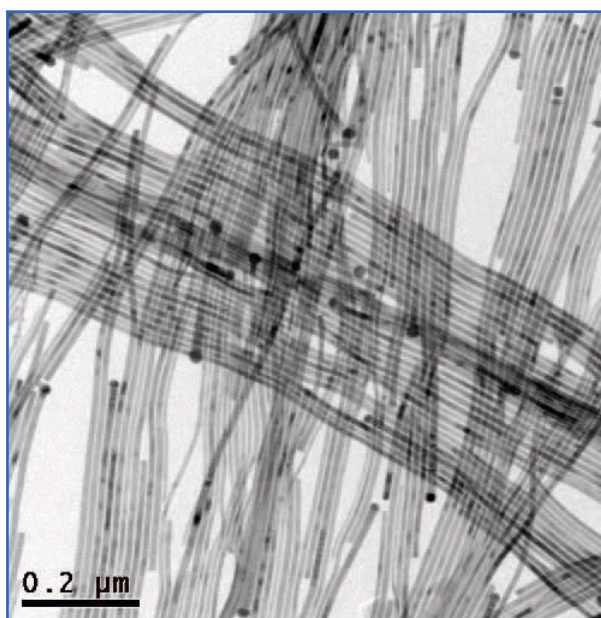
### Answers from the Past

Over the past twenty years, homogeneous nucleation in solution has proven to be an effective method for the synthesis of both metallic<sup>5</sup> and semiconductor nanocrystals.<sup>6</sup> Nearly isotropic, pseudospherical morphologies are typically produced. Other nanocrystalline morphologies are often desirable, and homogeneous nucleation has been adapted for the synthesis of rod-shaped morphologies.<sup>7</sup> However, the growth of nanowires by homogeneous nucleation is apparently limited to materials having particularly favorable, highly anisotropic crystal structures.<sup>8</sup> How then might nanowire morphologies be generally prepared?

The answer was uncovered by Wagner and Ellis in 1964,<sup>9</sup> who discovered that micrometer-scale silicon whiskers (wires) could be grown from gold-droplet catalysts under Chemical Vapor Deposition (CVD) conditions at about 1000 °C. The process was named the "Vapor-Liquid-Solid" (VLS) mechanism after the three phases involved. VLS growth was extended to micrometer-scale whiskers of many inorganic materials and intensively studied for over a decade, before fading into relative obscurity.

### From VLS to SLS

In 1995, my group reported that III-V semiconductor nanowires could be grown in solution from indium nanoparticle catalysts by a process analogous to the VLS mechanism, and by analogy we named it the "Solution-Liquid-Solid" (SLS) mechanism.<sup>10</sup> Shortly thereafter, Lieber and coworkers described laser-ablation adaptations of the VLS mechanism that afforded silicon and a wide range of other semiconductor nanowires (Laser-Assisted Catalyzed Growth, LCG).<sup>11-12</sup> Many others made seminal contributions to nanowire growth by VLS adaptations, most notably Korgel (Supercritical Fluid-Liquid-Solid, SFLS, mechanism)<sup>13</sup> and Yang.<sup>14</sup> We now routinely prepare soluble, III-V and II-VI semiconductor nanowires with controlled diameters in the strong-confinement regime of about 3–20 nm by bismuth-nanoparticle-catalyzed SLS growth (Figure 1).<sup>15-16</sup> The nanoparticle-catalyzed VLS mechanism and its solution-phase variants have emerged as *the* popular, widely practiced, general methods for the synthesis of semiconductor nanowires.<sup>17</sup> Gold nanoparticles are presently by far the most commonly employed catalysts.



**Figure 1.** CdTe nanowires grown by the SLS mechanism (Jianwei Sun, Washington University). The bismuth-nanoparticle catalysts are evident at the nanowire tips.

### Quantum Wires to Nanophotonics

The advantages of nanoparticle-catalyzed nanowire growth include its general applicability to a wide variety of materials, the diameter control afforded, the uniformity of the wires (lack of significant diameter fluctuations) and their oriented, near-single crystallinity. The surface passivation, solubility and length of the wires may also be systematically varied. Small-diameter "quantum" wires are ideal specimens for fundamental studies of two-dimensional (2D) quantum-confinement phenomena and for property comparisons to 3D-confined quantum dots, 1D-confined quantum wells and anisotropically 3D-confined quantum rods. Potential applications of semiconductor nanowires in nanophotonics and lasing, nanoelectronics, solar-energy conversion and chemical detection are under active development. Exciting progress and advances in the semiconductor-nanowire field, enabled by the emergence of nanoparticle-catalyzed growth, are anticipated in the immediate future.

**For gold nanoparticles, see page 7.**



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## Nanomaterials in Organic Photovoltaic Devices

Dr. Sean Dingman, Sigma-Aldrich Corp., Milwaukee, WI USA

The ability to create high-efficiency solar cells is a key strategy to meeting growing world energy needs. Nanotechnology is currently enabling the production of high-efficiency organic photovoltaics (OPVs) to help meet this challenge.<sup>18</sup> Organic photovoltaics are nanostructured thin films composed of layers of semi-conducting organic materials (polymers or oligomers)<sup>19</sup> that absorb photons from the solar spectrum. These devices will revolutionize solar energy harvesting, because they can be manufactured via solution-based methods, such as ink-jet or screen printing, enabling rapid mass-production and driving down cost.

OPVs currently lag behind their "inorganic" counterparts because of low solar energy conversion efficiencies (approximately 1-3%). Several research groups are addressing conversion efficiency by employing a combination of nanomaterials and unique nanoscale architectures. These hybrid organic-inorganic photovoltaics consist of light-absorbing polymers in contact with semiconductor nanocrystals, fullerenes or nanostructured metals. The nanomaterials affect electro-optical properties of the conducting polymer, which include assisting in absorption of red and near-IR photons, a significant portion of the solar spectrum. Examples of OPVs designs employing nanomaterials include:<sup>20-23</sup>

**Polymer-Fullerene Heterojunctions:** Cells where a chemically modified fullerene ( $C_{60}$ ) layer, acting as electron acceptors, is in close physical contact with a polymeric organic electron donor (MDMO-PPV catalog number **546461**, or poly-(3-hexylthiophene), P3HT, catalog number **445703** and **510823**). This contact improves efficiency by allowing charge transfer to take place at the sub 10-nanometer scale, on the order of the diffusion length of an exciton generated from organic semiconductors. The most recent cells exhibit conversion efficiencies of ~5%.

**Organic-Nanocrystal Solar Cells:** Blends of semiconducting polymers and semiconducting quantum dots or nanorods (CdSe or CdTe) are mixed in a manner similar to the polymer-fullerene blends. The polymers are modified to give rise to chemical bonding between the nanocrystal and polymer. The nanocrystals can be tailored to a wide variety of optical band gaps, which depend on the size of the nanocrystal (or the diameter of the nanorod).

**Dye-Sensitized Cells:** These cells employ complex dye molecules attached to the surface of nanostructured oxides like titanium(IV) oxide ( $TiO_2$ ) or niobium(V) oxide ( $Nb_2O_5$ ). The dyes exhibit broad light-absorption profiles and rapid photoinduced charge transfer of electrons to the nanocrystals. These cells show solar conversion efficiencies of ~4%.

**Tandem Cells:** The tandem cell acts as a 2-1 cell, harvesting photons from the complete visible spectrum. These cells employ layers of  $C_{60}$  as a strong blue light absorber and copper-phthalocyanine (CuPc) as a red-yellow absorber. Nanosized silver particles act as a charge conduit between the cells but do not absorb photons traveling through the cell because of their nanosized dimensions. These cells have achieved conversion efficiencies of ~6% (Figure 2).

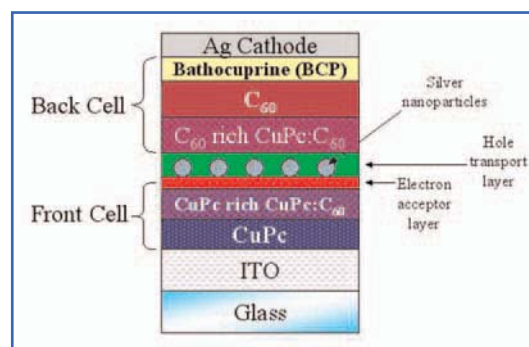


Figure 2. Schematic of tandem organic photovoltaic cells.<sup>24</sup>

Significant challenges exist to achieving OPV devices that can be mass-produced. Nanotechnology will assist in meeting the technical challenges of this rapidly evolving field.

Catalog #	Composition	Avg. Particle Size (nm)	Purity (%)
484059	Silver	100	99
576832	Silver	70	99.5

Sigma-Aldrich offers several grades of fullerenes for your materials applications.

Catalog #	Fullerene Type	Purity (%)	Catalog #	Fullerene Type	Purity (%)
572497	Fullerene soot, as produced (ca. 76% C <sub>60</sub> , 22% C <sub>70</sub> )	7	379654	(5,6)-Fullerene-C <sub>70</sub>	95
483036	Fullerene-C <sub>60</sub>	98	482994	(5,6)-Fullerene-C <sub>70</sub>	99
379646	Fullerene-C <sub>60</sub>	99.5	482951	Fullerene-C <sub>76</sub>	98
572500	Fullerene-C <sub>60</sub>	99.9	482978	Fullerene-C <sub>78</sub>	98
377120	Fullerite (ca. 90% C <sub>60</sub> , 10% C <sub>70</sub> )	—	482986	Fullerene-C <sub>84</sub>	98

Catalog #	Fullerene Type	Structure	Purity (%)	Catalog #	Fullerene Type	Structure	Purity (%)
64251	(1,2-Methano-fullerene C <sub>60</sub> )-61-carboxylic acid		97+	64247	Diethyl (1,2-methano-fullerene C <sub>60</sub> )-61,61-dicarboxylate		95+
64246	Ethyl (1,2-methano-fullerene C <sub>60</sub> )-61-carboxylate		95+	64248	Diethyl (1,2-methano-fullerene C <sub>70</sub> )-71,71-dicarboxylate		95+
64245	tert-Butyl (1,2-methano-fullerene C <sub>60</sub> )-61-carboxylate		95+				

## Coatings

Dr. Luke Grocholl, Sigma-Aldrich Corp., Milwaukee, WI USA

Nanopowders and nanoparticle dispersions have seen increasing applications in coatings. Due to their small size, very even coating can be achieved by painting nanoparticle dispersions onto a surface and baking off the residual solvent.

**Optically Transparent Conductive Coatings:** Indium tin oxide (ITO) and antimony tin oxide (ATO) are well known, optically transparent, electrically conductive materials. Nanoparticles of these materials can be painted on surfaces such as interactive touch screens to create a conductive, transparent screen without relying on expensive sputtering techniques. In addition, ITO and ATO can be used as an antistatic coating, utilizing their inherent conductivity to dissipate static charge.

**Optically Transparent Abrasion-Resistant Coatings:** Nanoscale aluminum oxide and titanium oxide are optically transparent and greatly increase the abrasion resistance of traditional coatings. Titanium oxide is of particular interest in many optical applications, since it is highly reflective for most ultra-violet radiation. Zinc oxide and rare-earth oxides are also UV-reflective, but optically transparent and are therefore effective in protecting surfaces from degradation brought about by exposure to UV radiation.

Catalog #	Composition	Avg. Particle Size (nm)
549541	Antimony tin oxide	19
544876	Indium tin oxide	25-45

Catalog #	Composition	Formula	Avg. Particle Size (nm)	Purity (%)
637262	Titanium(IV) oxide (rutile)	TiO <sub>2</sub>	10 X 40*	99.5
637254	Titanium(IV) oxide (anatase)	TiO <sub>2</sub>	5-10	99.7
634662	Titanium(IV) oxide (anatase)	TiO <sub>2</sub>	60-100	99.9
544906	Zinc oxide	ZnO	50-70	97.5
637289	Dysprosium(III) oxide	Dy <sub>2</sub> O <sub>3</sub>	60-100	99.9+
637343	Erbium(III) oxide	Er <sub>2</sub> O <sub>3</sub>	40-60	99.9+
634298	Europium(III) oxide	Eu <sub>2</sub> O <sub>3</sub>	60-100	99.5+
637335	Gadolinium(III) oxide	Gd <sub>2</sub> O <sub>3</sub>	40-60	99.9+
637327	Holmium(III) oxide	Ho <sub>2</sub> O <sub>3</sub>	40-60	99.9+
634611	Neodymium(III) oxide	Nd <sub>2</sub> O <sub>3</sub>	<40	99.9+
634263	Praseodymium(III,IV) oxide	Pr <sub>6</sub> O <sub>11</sub>	<125	99
637319	Samarium(III) oxide	Sm <sub>2</sub> O <sub>3</sub>	10-80	99.9+
634255	Terbium(III,IV) oxide	Tb <sub>4</sub> O <sub>7</sub>	60-100	99.5
637300	Ytterbium(III) oxide	Yb <sub>2</sub> O <sub>3</sub>	40-60	99.7+
544892	Yttrium(III) oxide	Y <sub>2</sub> O <sub>3</sub>	25-30	99

\* Average dimensions of crystallites



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## Carbon Nanotube-Based Biosensors

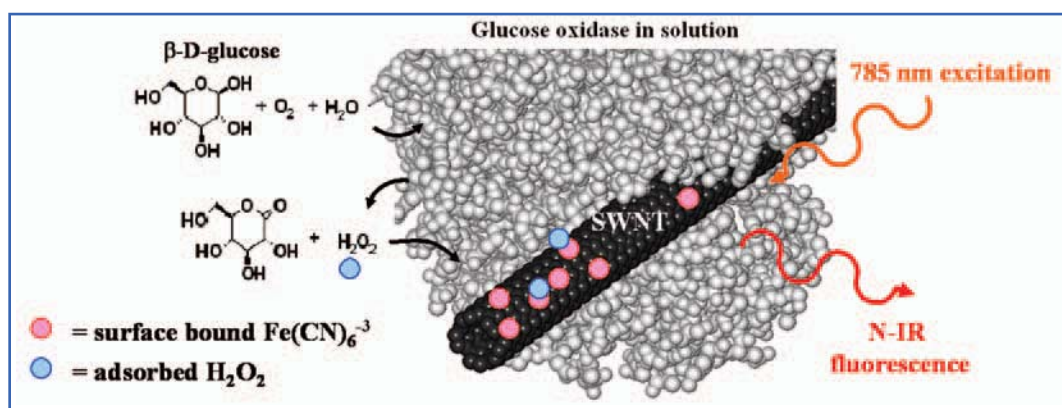
Prof. Michael Strano, Dr. Seunghyun Baik, Paul Barone, Department of Chemical and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL USA

### Bio-conjugates

Researchers from the University of Illinois at Urbana-Champaign have developed near-infrared optical biosensors based on single-walled carbon nanotubes, which modulate their fluorescence emission in response to specific biomolecules. The viability of sensor techniques was demonstrated by creating a single-walled carbon nanotube (SWNT) enzyme bio-conjugate that detects glucose concentrations.<sup>25</sup>

Carbon nanotubes fluoresce in a region of the near-infrared, where human tissue and biological fluids are particularly transparent to their emission. The sensor could be implanted into tissue, excited with a near-infrared light source, and provide real-time, continuous sensing of blood glucose level by fluorescence response. **Figure 3** shows a schematic mechanism of the nanotube sensor. Hydrogen peroxide is produced when glucose reacts with the enzyme, which quickly transforms ferricyanide to modulate near-infrared fluorescence characteristics of the nanotube.

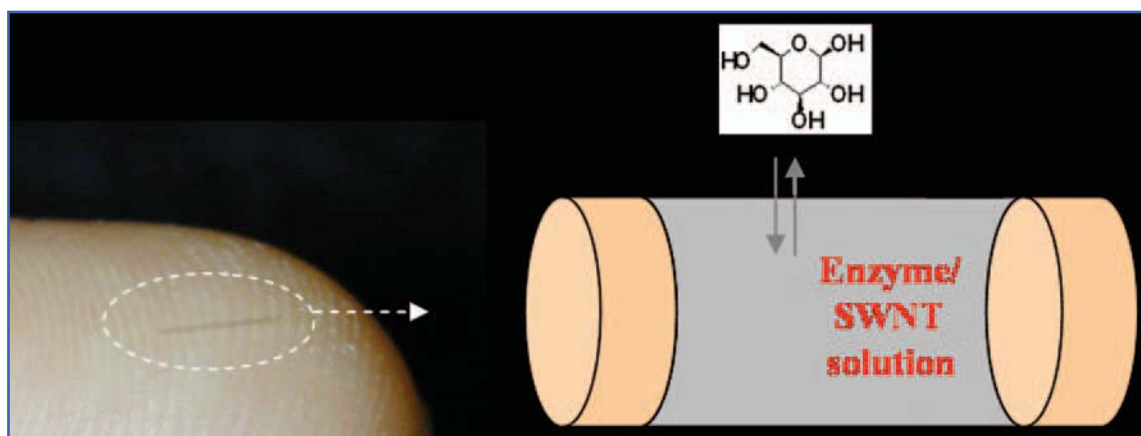
**Figure 3.** Near-IR radiation excites glucose to produce hydrogen peroxide ( $H_2O_2$ ). The reaction with surface-bound ferricyanide on the nanotubes modulates the fluorescence characteristics of the nanotube.



### Future Opportunities

The important aspect of this technology is that the technique can be extended to many other chemical systems. New types of non-covalent functionalization are developed, creating opportunities for nanoparticle sensors that operate in strong absorbing media of relevance to medicine or biology.

**Figure 4.** A size comparison of a SWNT-based glucose detector on a fingertip.



Sigma-Aldrich offers several grades of single-walled nanotubes for your applications.

Catalog #	Nanotube Type	Synthetic Method	Diameter (nm)	Length (nm)	Purity (%)
519308	Single-walled, CarboLex™ AP-grade	Arc	1.2-1.5	2-5	50-70
589705	Single-walled, as produced	Arc	0.9-1.2	10-30	12-15
652512	Single-walled, short	CVD	0.8-1.6	~0.5	90+
636797	Single-walled	CVD	0.8-1.6	0.5-100	90+

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## Layer-by-Layer Nanoassembly for Drug Delivery

Prof. Yuri Lvov, Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA USA

Researchers from Louisiana Tech University were among the pioneers of one of the novel nanotechnology methods: layer-by-layer (LbL) nanoassembly by alternate adsorption of oppositely charged polyelectrolytes, nanoparticles and proteins. With this technique, we can assemble ultrathin multilayers with nanometer precision and pre-determined composition across the film, and make nanocapsules from LbL films. We are using such nanocapsules for targeted drug delivery, biocompatible nanocoating and pulp microfiber processing. For this nanoarchitecture, we use nanoblocks, such as nanoparticles. In the development of our research area, we successfully used nanoparticles, such as different diameter and surface-charged gold nanoparticles, silica, nanoclay-montmorillonite, alumina, titanium dioxide and other nanoparticles. Also, we investigated linear polyelectrolytes of different types and molecular weight (especially natural polyelectrolytes), which we used as electrostatic glue to assemble nanoparticle and protein arrays. As any architect, we nanoarchitects need a wide palette of nanoblocks with new properties and dimensions, ideally, monodispersed, stable in solution, charged nanoparticles of noble metals, metal oxides and ceramics with diameters of 5, 10, 20, 50 and 100 nm.

Sigma-Aldrich offers gold nanoparticles and gold colloids as well as other aqueous nanoparticle suspensions.

Catalog #	Composition	Wt% Dispersion (in Water)	Formula	Avg. Particle Size (nm)	Purity (%)	pH	Conductivity (mS/cm)	Specific Surface Area (m <sup>2</sup> /g)
643092	Aluminum oxide	5	Al <sub>2</sub> O <sub>3</sub>	<20	99.9	4-5	100-400	>100
642991	Aluminum oxide	10	Al <sub>2</sub> O <sub>3</sub>	<20	99.9	4-5	100-500	>100
643130	Silicon dioxide, alumina doped	5	SiO <sub>2</sub>	<20	99.99+	5-7	<20	150-175
643084	Silicon dioxide, alumina doped	10	SiO <sub>2</sub>	<20	99.99+	5-7	30-40	150-175
643114	Titanium(IV) oxide	5	TiO <sub>2</sub>	<40	99.9+	2-3	400-800	20-40
643017	Titanium(IV) oxide	10	TiO <sub>2</sub>	<40	99.9+	2-3	600-1000	20-40

Catalog #	Material	Avg. Particle Size (nm)
636347	Gold nanopowder, 99.9%	50-130
G 1402	Gold nanoparticle, aqueous suspension*	3.5-6.5
G 1527	Gold nanoparticle, aqueous suspension*	8-12
G 1652	Gold nanoparticle, aqueous suspension*	17-23

\*Contains ~0.02 % NaN<sub>3</sub> as a preservative, <0.01% sodium citrate as a stabilizer, ~0.01 % HAuCl<sub>4</sub> and <0.01% tannic acid

## Antibacterial Applications

Dr. Luke Grocholl, Sigma-Aldrich Corp., Milwaukee, WI USA

Zinc oxide is an effective antibacterial and anti-odor agent. It has been used in deodorants, dental cleansers and diaper creams. The increased ease in dispersibility, optical transparency and smoothness make zinc oxide nanopowder an attractive antibacterial ingredient in many health care products. Copper oxide nanopowder has also been proposed as an anti-microbial preservative for wood or food products.

Catalog #	Composition	Formula	Avg. Particle Size (nm)	Purity (%)
544868	Copper(II) oxide	CuO	30-40	98
544906	Zinc oxide	ZnO	50-70	98.5



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## Nanomaterials in Fuel Cells

*Prof. Shelley D. Minteer, Department of Chemistry, Saint Louis University, St. Louis, MO USA*

Over the last two decades, general interest and research in fuel cells has increased, because they have the potential to be more energy efficient than conventional power generation methods.<sup>26</sup> During this time period, researchers have begun using nanomaterials in the catalyst layer of fuel cell electrodes for a variety of reasons, including: increasing the active surface area of the anode and cathode catalyst, increasing the catalytic rate of oxidation or reduction and minimizing the weight of platinum and other precious metals in the fuel cell. The current generated at an electrode is proportional to the active surface of catalyst on the electrode surface, so higher power density fuel cells can be formed from nanomaterials, because nanomaterials have a higher surface area to volume ratio. Researchers have also shown that the electrocatalytic properties of the materials are sensitive to particle size, so increased catalytic activity can be observed for nanoparticles and nanomaterials.<sup>27-29</sup> However, the most important goal has been to decrease the weight of platinum and other precious metals in the catalyst layer of the fuel cell, so that the fuel cell can be cost-effective. This has been the main limitation to the widespread use of fuel cells.<sup>26</sup> Researchers have employed carbon nanomaterials as supports for dispersions of platinum nanomaterials. This allows for a decrease in the weight of platinum needed to produce the same surface area of active platinum catalyst. The nanomaterials could be carbon foams containing nanopores,<sup>30</sup> different types of nanotubes<sup>31-32</sup> or even single-walled nanohorns.<sup>33</sup> All of these materials can act as a support and a conductor for platinum nanomaterials, making strides toward cost-effective fuel cell catalysts.

**For single-walled carbon nanotubes see page 6, for multi-walled carbon nanotubes see page 11.**

## Nanomaterials in Other Energy Applications

*Dr. Luke Grocholl, Sigma-Aldrich Corp. Milwaukee, WI USA*

### Environmentally Friendly Energy Sources

Devising schemes to meet the world's growing energy demands while simultaneously reducing green house emissions and other pollutants, has become one of the major challenges facing materials scientists. Nanomaterials promise to help solve many of the problems associated with new and emerging energy technologies.

**Fuel Cells:** Solid oxide fuel cells (SOFCs) offer the advantage over other fuel cell designs in that they do not require expensive, precious metal catalysts and can operate effectively without extensive purification of fuel sources. The activity of doped rare-earth oxide electrodes such as yttrium stabilized zirconia (YSZ) is directly related to their surface areas. Nanoparticles exhibit the high surface required for developing SOFC technologies.

**Cleaner Emissions:** Catalytic converters on vehicles around the world have significantly reduced the amount of automotive pollution over the last three decades. These devices require large amounts of expensive metals such as platinum, palladium and rhodium. Doped rare-earth metal oxides offer the promise of increased catalytic activity without the heavy reliance on precious metals. In addition, the increased efficiency of the next-generation catalytic converters will result in cleaner emission of existing internal combustion and diesel engines.

Catalog #	Composition	Dopant/ Stabilizer	Wt. % Stabilizer	Avg. Particle Size (nm)	Specific Surface Area (m <sup>2</sup> /g)
544760	Zirconium(IV) oxide			20-30	30-40
544779	Zirconium(IV) oxide	Yttria	10	20-30	30-40
572349	Zirconium(IV) oxide	Yttria	8	100	100-120
572322	Zirconium(IV) oxide	Yttria	3	100	100-120
572357	Cerium(IV) oxide	Gadolinium	20	100	100-120
572365	Cerium(IV) oxide	Samaria	15	100	100-120
572381	Cerium(IV) oxide	Yttria	15	100	100-120
572403	Cerium(IV) oxide	Calcium	10	100	100-120
572330	Cerium(IV) oxide	Gadolinium	10	100	100-120
575852	Cerium(IV)-zirconium(IV) oxide (3:1)			100	100-120

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## Nanotube-Polymer Composites for Ultra Strong Materials

Prof. Nicholas A. Kotov, Department of Chemical Engineering, University of Michigan, Ann Arbor, MI USA

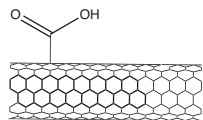
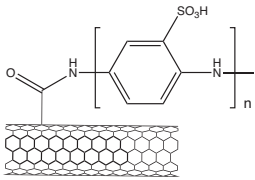
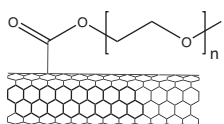
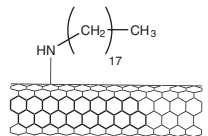
### Exceptional Strength

Exceptional mechanical properties of single-walled carbon nanotubes (SWNT) have prompted intensive studies of SWNT-polymer composites. However, the composites made with nanotubes are still holding a substantial reserve of improvement of mechanical properties. The problem is that pristine SWNTs have very poor solubility in polymers, which leads to phase segregation of composites. Severe structural inhomogeneities result in the premature failure of the hybrid SWNT-polymer materials. The connectivity with the polymer matrix and uniform distribution within the matrix are essential structural requirements for strong SWNT composites. This problem is being solved by several approaches. First, by using coatings from surfactants and polymers, such as sodium dodecyl sulfate or poly(styrenesulfonate). This enables formation of better dispersions in traditional solvents including water. Polymeric dispersion agents are strongly preferred for the composite preparation because of (a) tighter bonding with the graphene surface, (b) miscibility with polymer matrixes of composites and (c) substantially smaller concentration necessary for the preparation of SWNT dispersions. Among polymers, different poly(vinyl alcohols) work best as a host matrix for SWNTs, providing the composites with high tensile strength and excellent Young's modulus.

### Looking Ahead

An additional resource of SWNTs for improving the mechanical properties of composites is nanotube orientation. Virtually complete alignment of nanotubes can be achieved in SWNT composite fibers. These composites display substantially better mechanical properties than any other SWNT-polymer hybrid. If one can find a simple and controllable method to produce not only fibers but also bulk materials and coatings with nanotubes oriented in a desirable direction, new technological vistas can be opened for various composites. Breakthroughs in this area can come both from the studies of fundamental properties of SWNTs and from development of methods for composite processing. In the past, magnetic field alignment with exceptionally powerful electromagnets and alignment in the flow was used for this purpose.

Sigma-Aldrich offers single-walled nanotubes functionalized for enhanced processibility and better wetting characteristics.

Catalog #	Nanotube Type	Structure	Diameter (nm)	Length ( $\mu\text{m}$ )	CNT Purity (%)	Loading (%)	Solubility (mg/mL)
652490	Single-walled, carboxylic acid functionalized (3-6 atomic %)		4-5	0.5-1.5	80-90	3-6	H <sub>2</sub> O 0.1 DMF 1.0
639230	Single-walled, PABS (polyamino benzoic acid) coated (65 wt. %)		1.1	0.5-100	70-85	65	H <sub>2</sub> O 5.0 DMF 0.1 EtOH 0.05
652474	Single-walled, PEG (polyethylene glycol) coated (30 wt. %)		4-5	0.5-0.6	80-90	30	H <sub>2</sub> O 5.0
652482	Single-walled, ODA (octadecylamine) coated (30-40 wt. %)		2-8	0.5-1.0	80-90	30-40	THF >1.0 CS <sub>2</sub> >1.0 benzene >1.0 toluene >1.0 1,2-dichlorobenzene >1.0

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## Metal Matrix Nanocomposites for Structural Applications

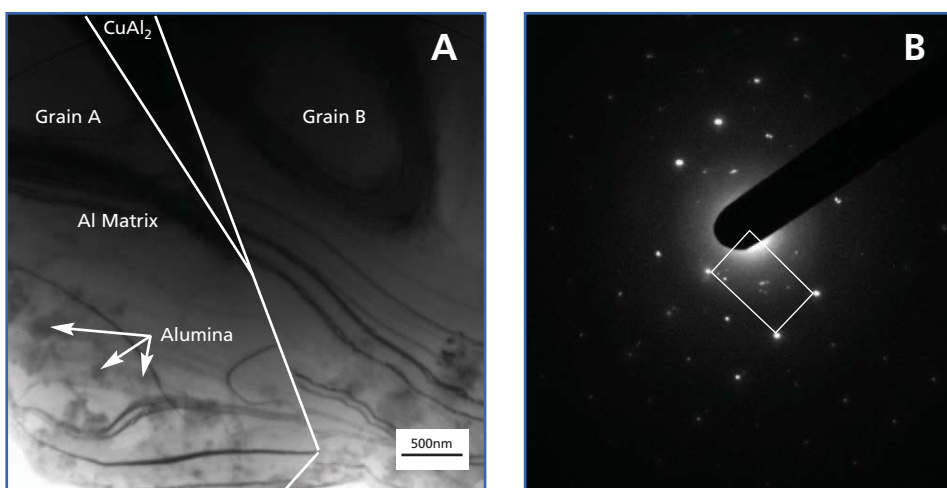
Prof. Pradeep K. Rohatgi; Ben Schultz; J.B. Ferguson, University of Wisconsin-Milwaukee Center for Composites, Milwaukee, WI USA

### Improved Properties

Metal matrix composites (MMCs) such as continuous carbon or boron fiber reinforced aluminum and magnesium, and silicon carbide reinforced aluminum have been used for aerospace applications due to their lightweight and tailorable properties.<sup>34</sup> There is much interest in producing metal matrix nanocomposites that incorporate nanoparticles and nanotubes for structural applications, as these materials exhibit even greater improvements in their physical, mechanical and tribological properties as compared to composites with micron-sized reinforcements.<sup>35-39</sup> The incorporation of carbon nanotubes in particular, which have much higher strength, stiffness, and electrical conductivity as compared to metals, can significantly increase these properties of metal matrix composites. Nanocomposites are being explored for structural applications in the defense, aerospace and automotive sectors.

### Low Cost Solutions

Concurrent with the interest in producing novel nanocomposite materials is the need to develop low cost means to produce these materials. Most of the prior work in synthesizing nanocomposites involves the use of powder metallurgy techniques, which are not only high cost, but also result in the presence of porosity and contamination.<sup>26, 40-41</sup> Solidification processing methods, such as stir mixing, squeeze casting and pressure infiltration are advantageous over other processes in rapidly and inexpensively producing large and complex near-net shape components, however, this area remains relatively unexplored in the synthesis of nanocomposites. Stir mixing techniques, widely utilized to mix micron size particles in metallic melts,<sup>42-43</sup> have recently been modified for dispersing small volume percentages of nanosize reinforcement particles in metallic matrices. Although there are some difficulties in mixing nanosize particles in metallic melts resulting from their tendency to agglomerate, a research team in Japan has published research on dispersing nanosize particles in aluminum alloys using a stir mixing technique.<sup>44</sup> Researchers at the Polish Academy of Science<sup>45</sup> have recently demonstrated the incorporation of greater than 80 volume percent nanoparticles in metals using high-pressure infiltration with pressures in the GPa range. Composites produced by this method possess the unique properties of nanosize metallic grains.



**Figure 5A.** Nanosize  $\text{Al}_2\text{O}_3$  particles embedded in cast aluminum matrix.

**Figure 5B.** Diffraction Pattern; the nanocomposite was synthesized at the University of Wisconsin, Milwaukee (TEM by Dr. M. Gajdardziska-Josifovska, Co-PI).

Recently, metal matrix nanocomposites were synthesized at the University of Wisconsin, Milwaukee using aluminum alloy A206 and nanoparticles of alumina ( $\text{Al}_2\text{O}_3$ ).<sup>46</sup> TEM samples of the cast Al-A206/ $\text{Al}_2\text{O}_3$  clearly show nanoparticles present within the metal matrix (Figure 5A). SAD patterns show the pattern of the matrix as well as the nanoparticles (Figure 5B). EDX indicates that the grains are composed of aluminum, which contains nanosize alumina particles. The distribution of particles throughout the grains of the matrix with an absence of large concentrations at the grain boundaries suggests wetting of the alumina by the liquid metal. In this case the nanoparticles did not appear to act as nucleation sites for nanosized grains.

Sigma-Aldrich offers several structural nanopowders as well as a variety of multi-walled nanotubes.

Catalog #	Nanotube Type	Synthetic Method	Outer Diameter (nm)	Inner Diameter (nm)	Length (nm)	Purity (%)
637351	Double-walled	CVD	<5	1.3-2.0	0.5-50	50-80 <sup>†</sup>
636819	Multi-walled, purified	CVD	<8	2-5	0.5-200	95+
412988	Multi-walled, as produced	Arc	6-20	*	1-5	8-10
406074	Multi-walled, powdered cylinder cores	Arc	6-20	*	1-5	30-40
636541	Multi-walled, purified	CVD	3-20	1-3	0.1-10	90+
636525	Multi-walled, purified	CVD	10-20	5-10	0.5-200	95+
636517	Multi-walled, purified	CVD	10-30	3-10	1-10	90+
636509	Multi-walled, purified	CVD	10-30	5-10	0.5-50	95+
636495	Multi-walled, purified	CVD	20-30	1-2 <sup>††</sup>	0.5-2	95+
636487	Multi-walled, purified	CVD	20-30	5-10	0.5-200	95+
636614	Multi-walled, purified	CVD	20-40	5-10	0.5-50	95+
636649	Multi-walled, purified	CVD	20-50	1-2 <sup>††</sup>	0.5-2	95+
636630	Multi-walled, purified	CVD	30-50	5-15	0.5-200	95+
636622	Multi-walled, purified	CVD	40-60	5-10	0.5-500	95+
636843	Multi-walled, purified	CVD	40-70	5-40	0.5-2	95+
636835	Multi-walled, purified	CVD	60-100	5-10	0.5-500	95+
636398	Graphite, nanofibers	CVD	80-200	0.5-10	0.5-20	95+

Catalog #	Composition	Formula	Avg. Particle Size (nm)	Purity (%)
544833	Aluminum oxide	Al <sub>2</sub> O <sub>3</sub>	40-50	98
551643	Aluminum oxide, whiskers	Al <sub>2</sub> O <sub>3</sub>	2-4 X 2800	99
594911	Silicon carbide (primarily beta-phase)	SiC	45-55	97.5
636967	Titanium carbide	TiC	130	98+
636940	Titanium carbonitride (C 7:N 3)	TiC <sub>0.7</sub> N <sub>0.3</sub>	<80	97+
636959	Titanium carbonitride	TiC <sub>0.5</sub> N <sub>0.5</sub>	<80	97+

<sup>†</sup>50-80% DWNT content, 10-40% other CNTs

<sup>††</sup> Wall thickness (microns)

\*8-30 graphene layers

## Books on Nanomaterials and Nanotechnology

### The Chemistry of Nanomaterials: Synthesis, Properties and Applications, 2 volumes (Catalog #Z703850)

C. N. R. Rao, A. Müller, A. K. Cheetham (Eds.), Wiley, 2004

With this handbook, the distinguished team of editors has combined the expertise of leading nanomaterials scientists to provide the latest overview of this field. The authors cover the whole spectrum of nanomaterials, ranging from theory, synthesis, properties, characterization and applications.

### Nanoparticles: From Theory to Applications (Catalog # Z551376)

G. Schmid (Ed.), Wiley, 2004

An introduction to the science of nanoparticles, from fundamental principles to their use in novel applications. As a basis for understanding nanoparticle behavior, the book first outlines the principles of quantum size behavior, nanoparticles architecture, formation of semiconductor and metal nanoparticles. It then goes on to describe the chemical syntheses of nanoparticles with defined characteristics, their structural, electrical and magnetic properties, as well as current methods to monitor these properties.

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