

**Analysis of the California Nanoindustry Focused on
Carbon Nanotubes and TiO₂ Nanomaterials.**

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EXECUTIVE SUMMARY

The State of California is a leader in nanotechnology with more than 20% of the U.S.-based micro and nano companies located in California. The largest nanotechnology industrial sector in California is the materials industry. Currently, most companies involved in California's developing nanoindustry are relatively small. Having been a leader and center for the high tech industry, California has an excellent infrastructure in place for development of this new and highly promising industry.

Within the major industrial sectors in California, a diverse range of nanotechnologies and applications have been or are being developed. The two most prominent types of nanotechnology identified in California are carbon nanotubes (CNTs) and titanium dioxide (TiO₂) nanoparticles. There are ten companies for carbon nanotubes and nine companies for titanium dioxide nanoparticles in California. However, only a company's headquarters or research facility is located California, while most manufacturing facilities are located in outside of California, in other states or overseas. No companies were found to make TiO₂ nanoparticles within California. California-based companies involved with TiO₂ nanotechnology have only a distribution function or are focused on research related to TiO₂ applications, and not manufacturing.

Major techniques for growth of carbon nanotubes are arc discharge, laser vaporization, and chemical vapor deposition (CVD). Carbon nanotubes are used to enhance the electrical conductivity and thermal property in plastic polymer composite materials. Conductive composite materials made with carbon nanotubes are being used in automotive parts, such as fuel line systems and conductive plastic exterior fenders. Lightweight and enhanced strength carbon nanotube composite materials are used for sporting goods such as tennis rackets, golf clubs, bicycle frames, and yacht parts. Transparent conductive films based on carbon nanotubes are used for touch screens, electrodes found in electronic display devices and electromagnetic interference shielding. The high thermal conductivity of carbon nanotube film has application as a thermal interface material in electronics.

Generally, TiO₂ nanoparticles are made by chloride processes such as sol-gel and hydrolysis, and are synthesized mainly from titanium tetrachloride (TiCl₄). TiO₂ nanomaterials can be used

for ultraviolet (UV) protection, photocatalysts, photovoltaics, photochromics, water treatment, anti-bacterial coating for medical devices, and air purification. Self cleaning products using the photocatalytic function and hydrophilic nature of TiO₂ nanomaterials are available in glass coatings for buildings, roofing and tents, automobile mirrors, road materials, and food preparations. Rutile structure TiO₂ nanoparticles are used in sunscreens because they are transparent and absorb ultraviolet (UV) radiation that damages the skin. Many types of sunscreen using TiO₂ nanoparticles are available in the market.

I. INTRODUCTION

Nanotechnology is a rapidly growing and highly diverse industry, holding great promise for new and improved products to enhance the quality of life. Likewise, the potential benefit to California's economy is great. Concerns, however, are also being expressed about the unknown toxicology and environmental fate of these newly developed nano-sized materials. Consequently, the Blue Ribbon task force report on nanotechnology recommended that Cal/EPA communicate with industry to promote responsible stewardship of nanotechnology products, take necessary actions before problems develop, and encourage responsible environmental applications of nanotechnology (Blue Ribbon).

To address these recommendations, a more detailed understanding of the current state of the California nanotechnology industry is needed. The purpose of this report is to review the current and potential future practices of the nanoindustry in California. This includes an inventory of the companies involved with nanotechnology and their operations in California, including the different technologies and applications as well as the potentially different types of nanomaterials and products produced and consumed.

This report investigates nanotechnology companies operating in California based on the type of nanotechnology and specific applications. A number of different nanotechnologies have been identified, including carbon-based nanomaterials, plastic-clay nanocomposites, metal matrix materials, quantum dots, cerium dioxide and gold catalysts, silver nanoparticles, titanium dioxide, nano-ink, and nano-lubrication materials. The distribution of companies involved with nanotechnology was determined in terms of the number of companies and their major products and applications within the different industrial sectors.

The report then focuses on carbon nanotubes (CNTs) and titanium dioxide (TiO₂) nanomaterials which were found to be the most widely used nanomaterials in California. These two nanotechnology areas have many diverse applications and currently have use in many available consumer products. Detailed information is provided on the identified companies, including nanomaterials or nanotechnology, products produced and fabrication methods, as well as the company's current operations in California. Furthermore, the report provides a comprehensive analysis on carbon nanotube and TiO₂ nanomaterials from the raw materials to their final applications to further an overall understanding of these key nanomaterials.

II. NANOTECHNOLOGY IN CALIFORNIA

2.1. Position of California nanotechnology industry in U.S.

The many innovative companies in electronics, materials and biotech give strength to California's technology leadership and economy. Furthermore, these industries possess the technology that can be directly applied to nanoscale products. The California semiconductor industry is an excellent example of a high-tech industry resource that has such capability for transition. In terms of numbers of nanotechnology companies, research, and economics, California leads the U.S. More than 20% of the U.S.-based micro and nano companies are located in California (Smalltimes 2007).

2.1.1 Distribution of nanotechnology industry

Figure 2.1 shows the distribution of nanotechnology companies in California for each industry sector. These industry sectors include materials¹, tools & instruments², electronics³, bio-health⁴, and energy⁵. The total number of companies (excluding venture capital and consulting companies) is 226. Additionally there are 29 research institutes⁶ including universities, private research centers, non-profit organizations, and government research centers in California.

The materials industry is the largest industry sector with 69 companies. The number of companies in the remaining five sectors ranged from 39 to 15. California has more research organizations than any other state with strong capabilities for providing theoretical support for development and application of nanotechnologies. The ten campuses of the University of California system, private universities, national research laboratories, and private research centers provide excellent resources and support for nanotechnology-related research and development. These resources and high tech infrastructure uniquely position California to become a leader in nanotechnology. Many of California's nanotech companies are small businesses that have limited funding. Given limited resources, a concern facing these small businesses is the unknown public health and environmental impacts of nanomaterials, as well as

¹ All types of nanoparticles, fibers, tubes, and thin films.

² Machines for characterization, surface analysis, thin film analysis etc.

³ Semiconductor chips and equip, displays, and micro(nano)electronic machine systems etc.

⁴ Medicines, bio-engineering, life science, and drug delivery etc.

⁵ Batteries, solar cells, and fuel cells.

⁶ Academics, government, and private research centers.

providing adequate health and safety for their workers when handling these materials in the research and development, and manufacturing environments.

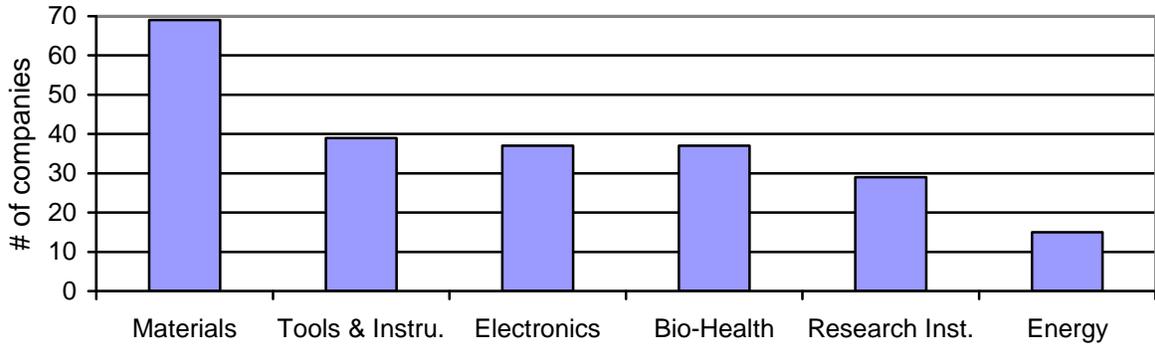
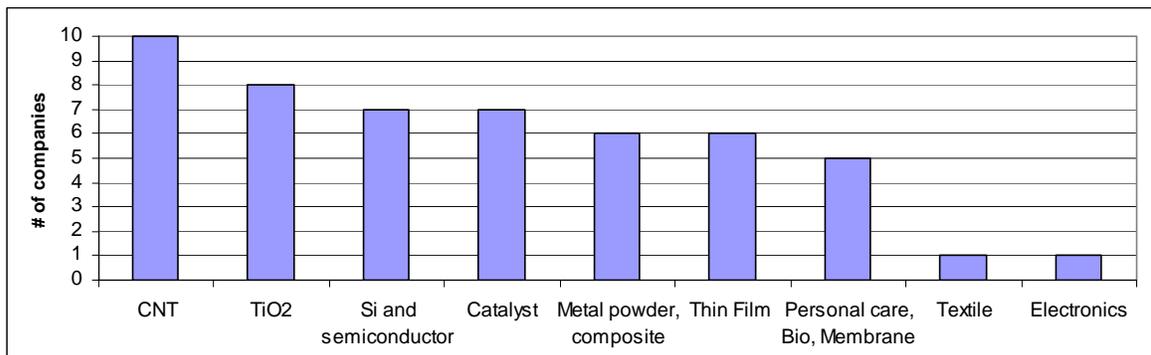


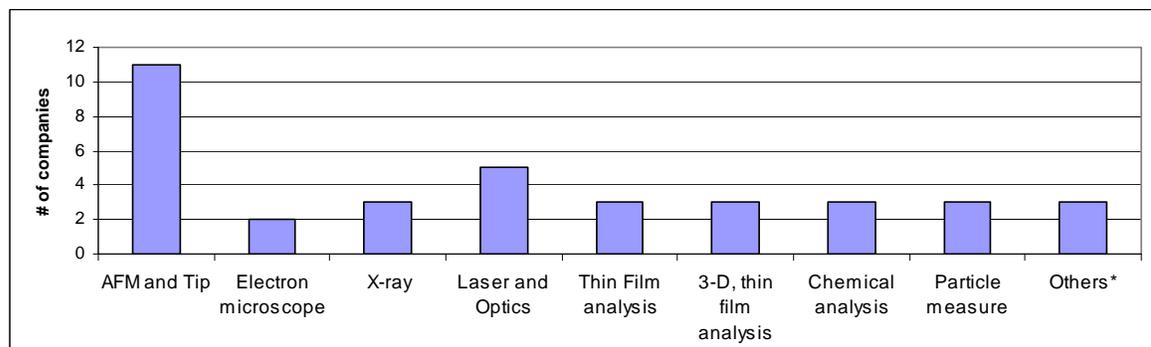
Figure 2.1 Distribution of companies in each industrial sector in California.

Figure 2.2 illustrates the major products in each industrial sector. The major products are carbon nanotubes in the materials sector (a), atomic force microscopy (AFM) tips in the tools and instruments sector (b), semiconductors in the electronics sector (c), sensors and diagnostic detection systems in the bio-health sector (d), and solar cells in the energy sector (e). A detailed listing of California nanotechnology companies and their products for each of the identified industrial sector are provided in Appendix I.

a)



b)



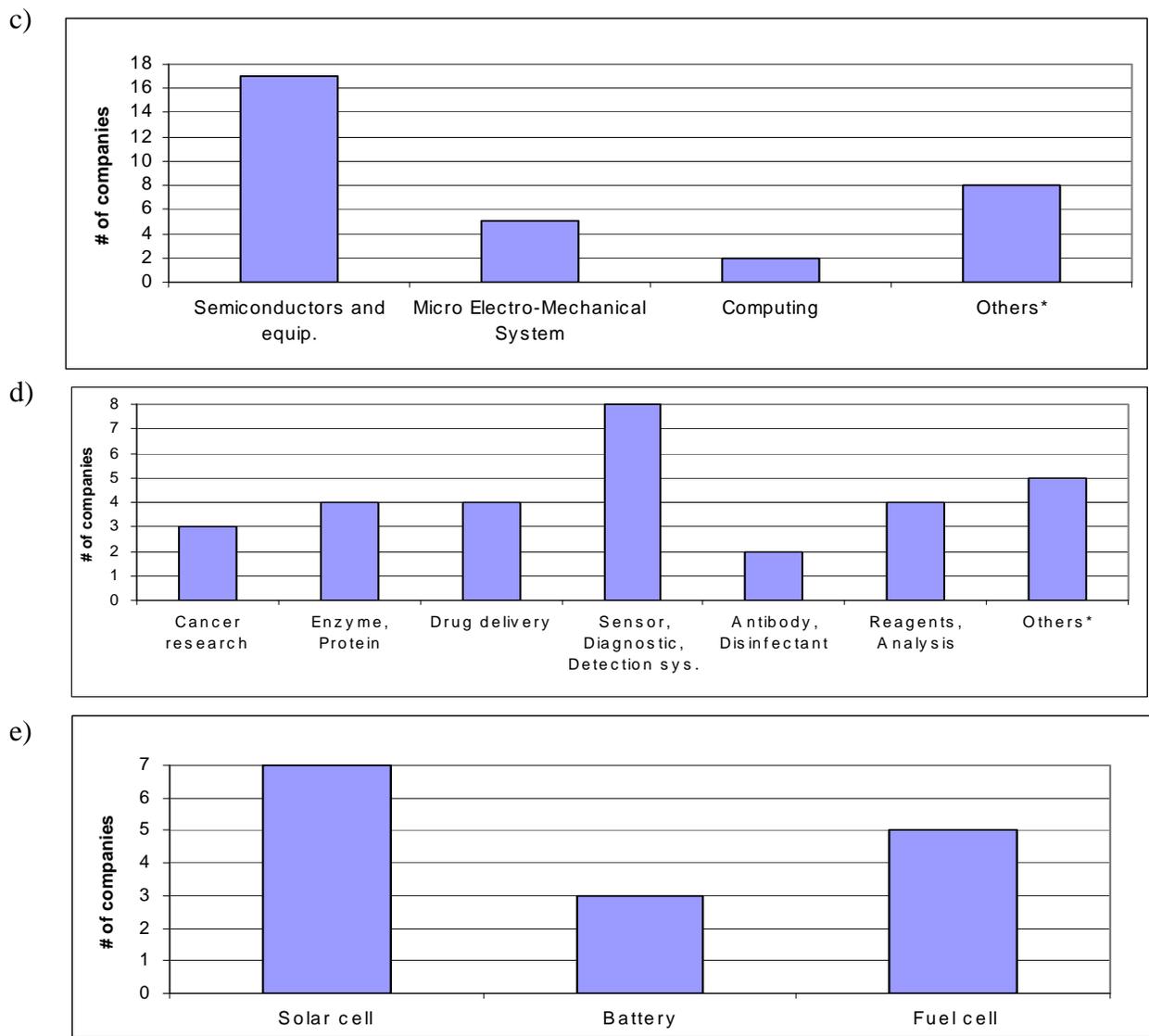


Figure 2.2 Major products in each industrial sector in California. (a) materials industry, (b) tools and instruments industry, (c) electronic industry, (d) bio-health industry, (e) energy industry.

2.2 Carbon nanotubes and TiO₂ nanoparticles industries in California

2.2.1 Carbon nanotubes

Carbon nanotubes have many applications ranging from plastic composites to atomic force microscopy (AFM) tips. There are 10 companies in California involved with carbon nanotubes, either directly or indirectly, one of which is at the R&D stage. All of these companies have a relatively short history, and most were established solely for newly found applications of carbon nanotubes. Only one of the 10 companies identified actually makes carbon nanotubes

commercially within California⁷. Although all 10 companies have offices in California, their manufacturing facilities are located outside of California, in other states or overseas, and only the company headquarters or distributorship is located in California. Additionally, a number of research institutes in California are known to produce carbon nanotubes for research purposes.

Chemical vapor deposition is primary method used to manufacture carbon nanotubes, which are typically shipped in a powder form. Eight of the ten companies are focused on manufacturing carbon nanotubes as a final product, while two companies use carbon nanotubes as raw material in manufacture of their products. Six of the companies manufacture other nanomaterials in addition to carbon nanotubes. Half (5) of the companies produce both single and multi-walled carbon nanotubes, while the other companies produce either only single-walled or multi-walled carbon nanotubes. Table 2.1 shows details on the carbon nanotube industry in California.

	Company Name	Location in CA	Business type		Production of CNT						
			Operation type	Comp. history	CNT Type	Shipping form	Manuf. site	Manuf. method	Raw materials	Final product	Other products
1	Ahwahnee, Inc	San Jose	User	2002	M	Powder	China	CVD	Gas with C	CNT	None
2	American Elements	LA	Marketing	-	S, M, D	Powder	China	-	-	CNT	QD, particles
3	Apex Nanomaterials	San Diego	Marketing	2003	S	-	China	Arc, CVD	Graphite	CNT	None
4	Carbon Solutions	Riverside	Producer	1998	S	Powder	CA	Arc	Graphite	CNT	None
5	Cnano	Menlo Park	Marketing	2006	S, M	Podwer	China	CVD	CH ₄ , Fe	CNT	Polymer
6	Molecular Nanosystems Inc	Palo Alto	R&D	2001	S, M	-	CA	CVD	Not open	CNT (?)	-
7	Nanomix Inc*	Emeryville	User	1997	S	Embedded	-	-	-	Biosensor	Biomonitor
8	Standford materials	Aliso Viejo	Marketing	-	S, M	-	China	-	-	CNT	TiO ₂
9	Sun Nano	Fremont	Marketing	-	S, M	Sol., Pow.	China	CVD	-	CNT	Particles
10	Unidym, Inc	Menlo Park	User	2000	S, M	Embedded	TX	HiPco, CVD	CO	Conduc. film	Fuel cell

Table 2.1 Carbon nanotube industry in California.

M: Multi walled, S: Single walled, D: Double walled. -: information is not available.

Marketing: makes product at other places (same company) and just sells the product. Producer: makes product at their own site. User: buys product from the manufacturer (same or other company) for use in their product. R&D: start-up phase, no sale of products.

2.2.2 TiO₂ nanoparticles

The TiO₂ nanoparticles industry in California is focused on application of TiO₂ rather than manufacturing. While there are companies that distribute TiO₂ nanoparticles in California, all known manufacturing facilities are located outside California. Similar to carbon nanotubes, the technology is relatively new and the involved companies have a short history⁸.

⁷ Except 1 R&D stage companies and one unconfirmed company.

⁸ Some companies that make conventional TiO₂ particles may have long history in general but a short history in nanotechnology since it is a relatively new industry.

Products containing TiO₂ nanoparticles have major application as a photocatalyst. The chloride process using TiCl₄ as the raw material is the primary method for producing TiO₂ nanoparticles. Because TiO₂ nanoparticles companies in California are a branch or satellite office of the manufacturing company, the specific fabrication methods were not confirmed. Although TiO₂ nanomaterials are typically produced in particle form, one company produces a film-type product. The form of product shipped varies from solutions to thin film and powders. Most companies that produce TiO₂ nanoparticles also produce other nanomaterials. Similar to carbon nanotubes, it is expected that some research institutes make TiO₂ nanoparticles for research purposes. Details of the TiO₂ nanomaterial industry in California are listed in Table 2.2.

	Company Name	Location in CA	Business type		Production of TiO ₂						
			Operation ^o	Comp. history	Product Type	Particle size (nm)	Shipping form	Manuf. site	Purchase TiO ₂ from	Final product	Other products
1	American Elements	LA	Marketing	2006	Particle	10 ~ 200	Sol., powder	China	N/A	TiO ₂	Powder
2	Green Millenium, Inc	San Dimas	Marketing	2003	Particle	10	Solution	Japan	Saga-Kon	TiO ₂	N/A
3	Green Nanolife, Inc	La Palma	Marketing	2007	Particle	~ 10	Solution	Korea	Lexon	TiO ₂	Ag, Au
4	Ishihara Corp. USA	SF	Marketing	-	Particle	7 ~ 50	Sol., powder	Japan	Isihhara	TiO ₂	ZnO, ZrO ₂
5	Oxonica Inc.	Mount. View	User	1999	Particle	70	Cream	Europe	Third party	Sun screen	CeO ₂
6	MTI corporation	Richmond	Marketing	1995	Particle	5~ 50	Powder	China	N/A	TiO ₂	Powder
7	Pilkington	Lathrop	Marketing	2001	Thin Film	15	Thin Film	IL	N/A	Gass	N/A
8	Stanford materials	Aliso Viejo	Marketing	-	Particle	-	-	-	-	TiO ₂	SiO ₂
9	Sun Nano	Fremont	Marketing	-	Particle	5 ~ 55	Sol., powder	China	-	TiO ₂	Powder

Table 2.2 TiO₂ nanomaterial industry in California.

Marketing: makes product outside California (same company) and just sells the product. User: buys product from manufacturer (same or other company) for use in their product. -: information is not available.

III. CARBON NANOTUBES

Since their discovery, carbon nanotubes have been found to have extraordinary properties compared to conventional materials. Because of their great potential for a diverse range of applications, carbon nanotubes have been the most intensively researched nanomaterial. They can be used for electronics, composite materials, batteries, solar cells, sensors, semiconductors, and tips for scanning instruments.

3.1 Fabrication methods

The primary methods for fabrication of carbon nanotubes are arc discharge, laser vaporization, and chemical vapor deposition. High pressure carbon monoxide (HipCO) (Yang 2002), electrospinning (McCann 2007), and template methods that use anodic aluminum oxide (Wu 2004) are also used to make carbon nanotubes.

3.1.1 Arc discharge

Arc discharge is a common method used to produce carbon nanotubes. In vacuum condition, with ambient gas (helium (He), argon (Ar), or methane (CH₄)) at desired pressure, DC or AC arc voltage is applied between the two graphite electrodes. When pure graphite rods are used, the anode is consumed and multi-walled carbon nanotubes (MWCNTs) are deposited on the cathode. The majority of the anode evaporates to form fullerenes, which are deposited in the form of soot in the chamber, while a small part of the anode evaporates to form multi-walled carbon nanotubes that are deposited on the cathode. Figure 3.1 illustrates the arc discharge method for making carbon nanotubes.

For multi-walled carbon nanotubes, a gas containing hydrogen atoms is more effective than an inert gas, such as helium or argon (Ando 2004; Saito 2000). Methane gas (CH₄) was found best for forming multi-walled carbon nanotubes with high crystallinity and few coexisting carbon nanoparticles (Ando 1994). It also has been reported that fullerenes cannot be formed in a hydrogen-containing gas (Tai 1994), which is the basic difference between carbon nanotube and fullerene production.

Generally, arc discharge multi-walled carbon nanotubes are typically more than 10 μ m long and around 10 to 50 nm in diameter. The number of walls is limited to less than 30. Multi-walled

carbon nanotubes produced by arc discharge are highly crystalline and exhibit fewer defects than those produced by other methods (Grobert 2007; Saito 2000).

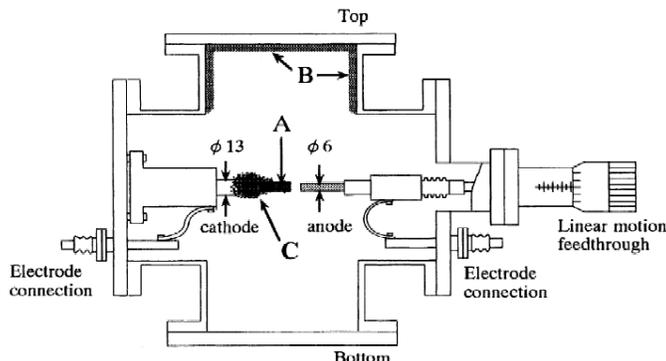


Figure 3.1 Schematic diagram of arc discharge apparatus. Multi-walled carbon nanotubes are deposited on A and single-walled carbon nanotubes are deposited on B and C as a form of soot (Saito 2000).

To produce single-walled carbon nanotubes (SWCNTs) using the arc discharge method, a graphite rod anode that contains a catalyst metal, such as iron (Fe), cobalt (Co), nickel (Ni), or yttrium (Y) is required. Single-walled carbon nanotubes are then generated in the form of soot on chamber wall and at the base of the cathode electrode. The maximum yield is achieved with a Ni-Co alloy catalyst. Table 3.1 lists catalysts that are used in producing single-walled carbon nanotubes and Table 3.2 shows one example of synthesis conditions for carbon nanotubes in an arc discharge process (Saito 2000).

Catalyst metal	Production method	Catalyst metal	Production method
Co	Arc	Rh-Pt	Arc
Ni	Arc	Y	Arc
Fe-Ni	Arc and laser	La	Arc
Co-Ni	Laser	Ni-Y	Arc
Rh	Arc	Ni-Na	Arc

Table 3.1 Typical catalysts commonly used for synthesizing single-walled carbon nanotubes (Saito 2000).

Power	DC or AC	Pressure	50 ~ 200 Torr	
Anode	6 mm in diameter	Electrode temperature	Anode	4000 K
	50 mm length		Cathode	3500K
Cathode	10 ~ 13 mm in diameter	Gap between electrodes	1 mm	
Current	70 A	Voltage	20 V	

Table 3.2 Operational conditions for arc discharge method (Saito 2000).

Generally, it is hard to grow aligned carbon nanotubes by arc discharge, i.e. growth directions are random. However, the growth temperature of the arc discharge method is higher than that of other carbon nanotubes production methods. As a result, the crystallinity and perfection of arc discharge produced carbon nanotubes are generally high, and the yield per unit time is also higher than other methods. Arc discharge can produce larger amounts of single-walled carbon nanotubes than the laser evaporation method. However, single-walled carbon nanotubes produced by arc discharge contain impurities such as amorphous carbon, polyhedral carbon, and catalytic metal particle (Grobert 2007; Ando 2004; Saito 2000).

3.1.2 Laser evaporation

In this method laser power vaporizes a graphite target. Figure 3.2 shows a schematic diagram of the laser furnace method developed by Smally's group (Ando 2004). A laser beam (Nd-YAG ($Y_3Al_5O_{12}$) or CO_2) is focused onto the target, which is doped with catalytic metals. The target is vaporized in a high-temperature inert gas environment (Ar or He) and single-walled nanotubes formed are collected in a water-cooled trap. At first, the graphite vapor is converted into amorphous carbon. Homogeneous annealing of the amorphous carbon then makes for high crystallinity single-walled nanotubes.

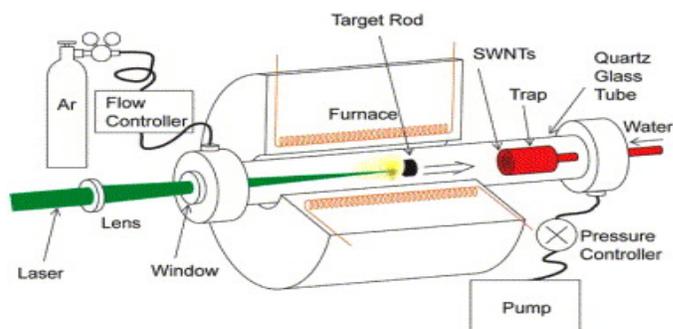


Figure 3.2 Schematic diagram of the laser furnace system for carbon nanotubes (Ando 2004).

Generally, Ni, Co, and Pt are used as catalysts. Due to amorphous carbon and catalytic metal byproducts a purification process, such as oxidation and filtration, is required. The laser evaporation favors the growth of single-walled carbon nanotubes, i.e. multi-walled carbon nanotubes are generally not generated with this method. The quality and properties of single-walled carbon nanotubes produced by this method are considered comparable with those of single-walled carbon nanotubes grown by arc discharge (Grobert 2007).

3.1.3 Chemical vapor deposition (CVD)

Chemical vapor deposition is a well known technique in the semiconductor and microelectronic industry. To grow carbon nanotubes using this process, carbon containing gases pass through the furnace in which catalyst materials are present at a temperature of 600 ~ 1200°C. The major parameters for carbon nanotubes growth in CVD are hydrocarbon gas as a carbon source, catalyst, and growth temperature. As carbon sources, carbon monoxide (CO), methane (CH₄), acetylene (C₂H₂), ethylene (C₂H₄), and alcohol are used. Transition metals such as Fe, Co, and Ni are used as the catalyst for carbon nanotubes growth. Figure 3.3 is a schematic diagram of a chemical vapor deposition system for carbon nanotubes.

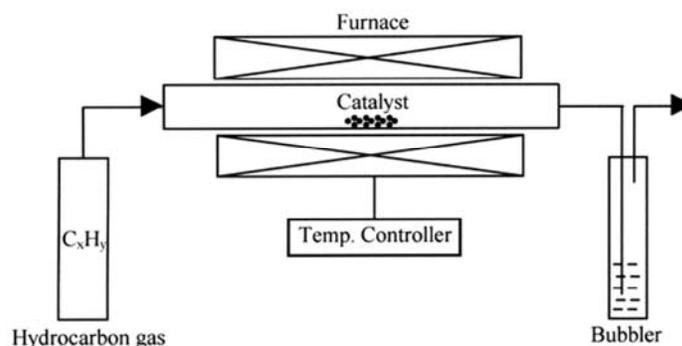


Figure 3.3 Schematic diagram of chemical vapor deposition system.

Generally, a high reaction temperature (900 ~ 1200°C) is needed for single-walled carbon nanotubes growth, while a low reaction temperature is needed (600 ~ 900°C) for multi-walled carbon nanotubes growth. Whereas multi-walled carbon nanotubes can grow from a mixture of most carbon-containing gases and an inert gas⁹, single-walled carbon nanotubes can only be grown from carbon-containing gases such as CO, CH₄, etc. These gases have a reasonable stability in the temperature range of 900 ~ 1200°C, in a mixture with H₂ and an inert gas such as Ar (Ando 2004; Grobert 2007).

The CVD method for producing carbon nanotubes includes two steps. The first step is coating the catalyst material such as Fe, Ni, and Co on the substrate by sputtering or other methods. The catalyst layer is then annealed or etched. Annealing of the metal layer makes

⁹ Common precursors for MWCNTs such as C₂H₂, C₂H₄ are unstable at high temperature and lead to deposition of impurities such as carbonaceous compounds (Ando 2004).

clusters, which are sites for nucleation of carbon nanotubes. Otherwise, ammonia gas (NH₃) is generally used to etch out the catalyst metal layer and provide nucleation sites.

The second step is the actual growth of carbon nanotubes on the substrate. When the substrate-catalyst interaction is strong, carbon nanotubes grow up with the catalyst particle rooted at its base (base growth model). On the other hand, when the substrate-catalyst interaction is weak, the catalyst metal particle is lifted up by the growing carbon nanotube (tip growth model). Figure 3.4 shows base growth model of carbon nanotubes.

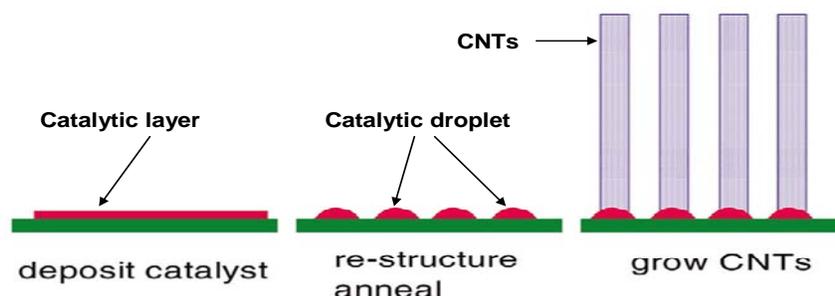


Figure 3.4 Schematic diagram of base growth model of carbon nanotubes (Robertson 2007).

In CVD process, formation of single-walled carbon nanotubes or multi-walled carbon nanotubes can be controlled by the size of the catalyst particle. Broadly speaking, when the particle size is a few nanometers, single-walled carbon nanotubes form, whereas particles a few tens of nanometers wide favor multi-walled carbon nanotubes formation (Ando 2004).

CVD is the best process to grow aligned carbon nanotubes on desired substrates for specific application. This is not feasible with arc discharge or laser evaporation methods. CVD is the most suitable process for generating doped carbon nanotubes, e.g., with Boron (B), Nitrogen (N), or both. Also, carbon nanotube production with CVD is easy to scale up and economic. However, CVD grown multi-walled carbon nanotubes are usually less crystalline and exhibit many more defects than arc-discharge multi-walled carbon nanotubes (Grobert 2007; Ando 2004). Table 3.3 below shows typical chemical vapor deposition conditions for growth of carbon nanotubes.

Reaction gas	Carbon containing gas (CH ₄ , CO, C ₂ H ₂ etc.)	Catalyst:	transition metals (Fe, Ni, Co, etc.)
Temperature	600 ~ 1200°C	Substrate	Si wafer, SiO ₂
Pressure	~8 X 10 ⁻⁶ Torr	Power	Thermal, plasma, laser
SWCNT growth	Ar, H ₂		

Table 3.3 Process conditions for carbon nanotubes growth in CVD (Ando 2004; Grobert 2007).

3.2 Properties of carbon nanotubes

3.2.1 Generic characteristics

Carbon nanotube is a tubular form of carbon with diameter as small as few nm and length of few nm to μm range. The ideal carbon nanotube is a graphene sheet rolled into a cylindrical shape that is closed at each end by half of a fullerene. Single-walled carbon nanotubes have three different structures based on rolling direction.

- Zigzag: two opposite C-C bonds of each hexagonal are parallel to the tube axis.
- Armchair: two opposite C-C bonds of each hexagonal are perpendicular to the axis.
- Chiral: two opposite C-C bonds of each hexagonal lie at an angle to the tube axis.

The electrical property of single-walled carbon nanotubes differs according to direction of rolling. Carbon nanotubes are the strongest and most flexible molecular material due to the C-C covalent bonding and seamless hexagonal network architecture (Meyyappan 2004). Figure 3.5 shows schematic diagrams of the three different types of single-walled carbon nanotubes. Carbon nanotube dimensional properties are summarized in Table 3.4 (Dong 2007).

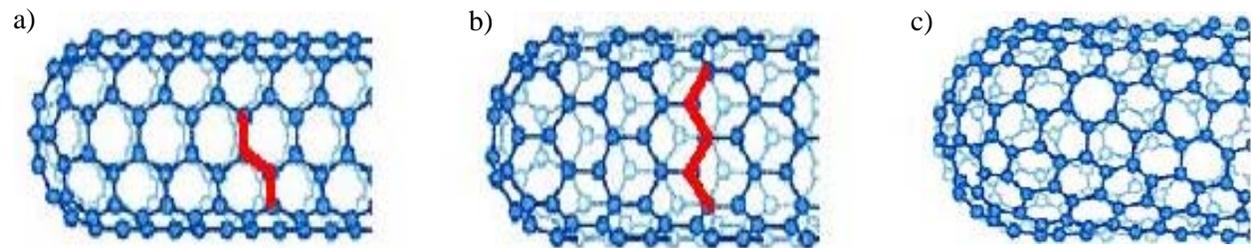


Figure 3.5 Types of single-walled carbon nanotubes according to rolling direction. a) arm chair, b) zigzag, c) chiral (CWRU).

Layers	Single/Multiple
Aspect ratio	10 ~ 1000
Diameter	0.4 ~ 3 nm (Single-walled carbon nanotubes) 1.4 ~ 100 nm (Multi-walled carbon nanotubes)
Length	Several micrometers

Table 3.4 Some geometrical properties of carbon nanotubes.

3.2.2 Thermal properties

Carbon nanotubes have a thermal conductivity¹⁰, k , of about 3kW/mK (Hone 2004) (diamond: 2 kW/mK) in the axial direction with small variation in the radial direction, and a high

¹⁰ The ability of a material to transfer heat, [W/m.K].

temperature stability of 750 ~ 3000°C. Generally, the thermal property is dependent on the type of tube, catalyst and fabrication method (Begtrup 2007; Kim 2004).

3.2.3 Mechanical properties

Carbon nanotubes have a very low density, 1.4 g/cm³ (Al: 2.7 g/cm³) and a strength to weight ratio about 500 times greater than aluminum, steel or titanium. Table 3.5 lists the Young's modulus and tensile strength of carbon nanotubes which are on the order of Tera pascals (TPa)¹¹ although this varies based on type of carbon nanotubes and fabrication method (Bacsa 2007).

Young's modulus	0.01 ~ 1.8 TPa	Multi-walled carbon nanotubes
	1.25 TPa	Single-walled carbon nanotubes
Tensile strength	0.01 ~ 0.15 TPa	Multi-walled carbon nanotubes
	-	Single-walled carbon nanotubes

Table 3.5 Young's modulus and tensile strength for carbon nanotubes (Grobert 2007).

3.2.4 Electrical properties

Multi-walled carbon nanotubes will be conductive, except if they have very few walls, while single-walled carbon nanotubes can be semiconductors or conductive (Robertson 2007). Current density of carbon nanotubes is 10⁷ ~ 10⁹ A/cm² (Cu: 10⁶ A/cm²). Carbon nanotubes with a high aspect ratio and small tip radius of curvature show good field emitting properties (emission of electrons) because of their sharpness.

Both single-walled and multi-walled carbon nanotubes show a low field emission voltage of 1 ~ 3 V/mm (Si, Mo: 50 ~ 100 V/mm) (Bacsa 2007). Figure 3.6 shows the rapid increase in conductivity corresponding to the percolation threshold¹². Very low threshold values are possible for multi-walled carbon nanotubes, i.e. similar electrical effect can be seen with fewer amounts of carbon nanotubes than convention fillers such as carbon blacks.

¹¹ The tensile strength of 304 stainless steel: ~ 500MPa

¹² Percolation means a sharp transition or an infinite network at which long-range conductivity suddenly appears. It is a critical factor in electrical conductivity of composite materials.

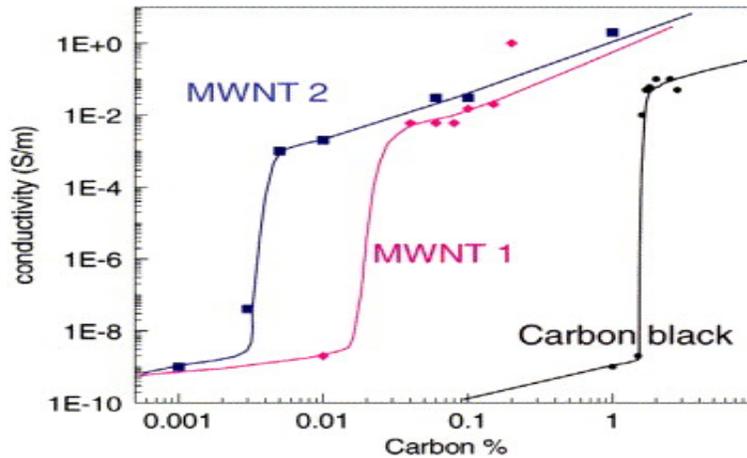


Figure 3.6 Conductivity versus carbon content for three different carbon/epoxy composite systems (Robertson 2004).

3.3 Pretreatment of carbon nanotubes

3.3.1 Purification

As produced, carbon nanotubes contain some foreign materials or impurities such as metal catalyst particles, soot, and carbon nanoparticles. The purpose of purification is to remove these impurities and obtain the highest yield without damage to the nanotubes. Oxidation by hot air, acid treatment by hydrofluoric acid (HF), nitric acid (HNO₃) or hydrochloric acid (HCl), centrifugation, filtration, and surfactant processes are used for purification of carbon nanotubes (Saito 2000; Ando 2004; Zheng 2002). Figure 3.7 shows one example of a detailed single-walled carbon nanotube purification process. The extraction with toluene removes fullerenes and soluble impurities. H₂O₂ (hydrogen peroxide) is then used to remove the amorphous carbon. The acid treatment gets rid of metal catalyst particles and finally purified single-walled carbon nanotubes are obtained through filtration and air drying.

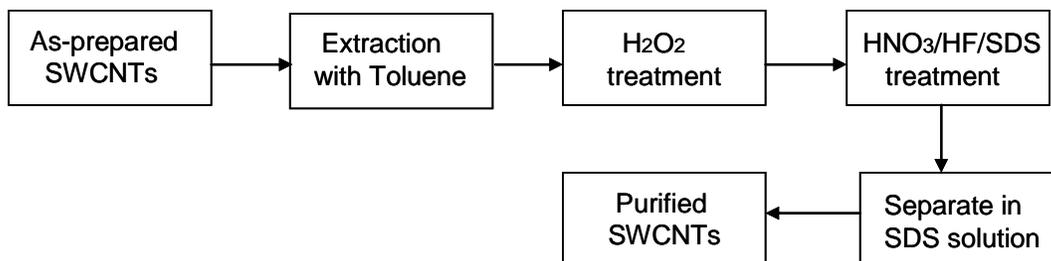


Figure 3.7 A flow process for purification of single-walled carbon nanotubes. SDS: sodium dodecyl sulphate (modified from Montoro 2006)

To purify multi-walled carbon nanotubes, gas-phase oxidation is commonly used after removal of metal catalyst particles by HF treatment. Air, O₂, Cl₂, or mixtures of these gases are used in a temperature range of 300-600°C (Shanov 2006; Ebbesen 1994; Montoro 2006).

3.3.2 Functionalization

Physical or chemical treatments are used to modify the surface property of carbon nanotubes as needed for specific applications. Technically, functionalization is a process that creates defects or oxides on the ends and sidewalls of the nanotubes which otherwise would be chemically inert and non-reactive like graphite.

Functionalization enhances adsorption (or physisorption) of molecules on the sidewalls or tips of single or multi-walled carbon nanotubes. Chemical modification of the sidewall may also improve the adhesion characteristics of carbon nanotubes in a host matrix to make composites. Processes used to functionalize carbon nanotubes include chlorination (Chen 1998), fluorination (Michelson 1998), and glow discharge (Khare 2002). The adsorbed molecules adhere to the nanotube surface by intermolecular forces. Through functionalization, biological species can be bonded covalently to the defect sites. Additively, coating or wrapping nanotubes with polymers make the nanotubes water soluble or biocompatible (Yun 2007).

3.3.3 Dispersion

Due to physical interaction, carbon nanotubes agglomerate, reducing their available surface area. Carbon nanotubes must be well dispersed to maximize contact and transfer of their properties to a composite material, i.e. agglomerates have to be broken up. Dispersions of carbon nanotubes can be obtained by mechanically reducing the agglomerate size and adding special dispersing agents such as polyvinylpyrrolidone (PVP) or sodium dodecyl benzene sulfonate to prevent the nanotubes from re-agglomeration.

3.4 Applications of carbon nanotubes

3.4.1 Carbon nanotubes/polymer composite materials

Carbon nanotubes are used to enhance the electrical conductivity and thermal properties of plastic polymer composite materials. The higher aspect ratio of carbon nanotubes (1000:1) allows equivalent conductivity at lower loading compared to conventional conductive fillers such as carbon black or carbon fiber. The price of carbon nanotubes is still expensive compared to

other materials¹³, restricting their potential use. Even so, the U.S. automotive industry has used conductive carbon nanotube composite materials in fuel systems and other parts since the late 1990's (PT 2004).

3.4.1.1 Fabrication methods for carbon nanotubes/polymer composite materials.

In solution based methods, carbon nanotubes are dispersed in the solution and mixed with the solution of polymer. Both aqueous and organic solvent solutions are available. The carbon nanotubes/polyvinyl alcohol and carbon nanotubes/polystyrene composite materials can be made by this method. In order to make composite materials using thermoplastic polymers such as high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) and polypropylene melt processes can be used. After mixing carbon nanotubes and polymers, heat is applied to melt the polymers and then injection molding can be used to make the required forms. The other fabrication process for composites is *in situ* polymerization. Monomers are used in the process and polyaniline, polystyrene and polyimide composite materials can be made by this process (Harris 2004).

An unfortunate consequence of composite materials is decreasing ductility after adding the fillers. Nanotubes preserve more of the neat resin's elongation at break strength compared to carbon black and carbon fiber. Also, low gasoline vapor permeability of carbon nanotube composite materials increases their use in automotive fuel line systems. Table 3.6 shows the property changes achieved with addition of some commercially available fillers in PC/ABS composites (Rich 2002).

Resin types	Loading (wt%)	Surface resistivity (ohm)	Volume resistivity (ohm-cm)	Elongation at break (%)	Surface roughness (μm)
PC/ABS*	-	N/A	10 ¹⁶	100	0.019
PC/ABS + MWCNT	7.3	10 ⁴ ~ 10 ⁶	10 ¹ ~ 10 ³	10+	0.025
PC/ABS + Carbon Black	16.7	~10 ⁶	~10 ³	3	0.035
PC/ABS + Carbon Fiber	13.7	~10 ⁶	~10 ³	1~3	0.426

Table 3.6 Change of properties in nanocomposite material with different types of fillers.

*: Polycarbonate/Acrylonitrile butadiene styrene.

¹³ The price depends on types and purity of tubes. Single-walled carbon nanotubes: \$45~\$200/g, Multi-walled carbon nanotubes: \$5~\$50/g as of 11/2008 (Cheaptubes).

To use carbon nanotubes in composite materials, functionalization is necessary to modify their surface properties. This is done to avoid phase separation, aggregation, and poor adhesion with the matrix as well as to enhance the interaction between carbon nanotubes and the matrix. Figure 3.8 shows one example of functionalization of carbon nanotubes for composite materials.

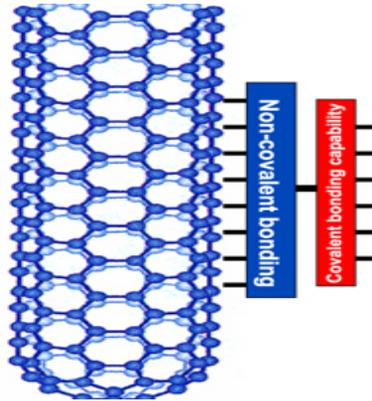


Figure 3.8 Functionalization of CNT surface (Zyvex).

3.4.1.2 Automotive parts

Carbon nanotubes filled conductive polymer composite materials are being used in several automotive parts. One application is the fuel line system which must be conductive to prevent buildup of electrostatic charges, a fire and explosion hazard. In this application, the electrical conductivity of carbon nanotubes is a desirable property, and a low loading of carbon nanotubes can achieve the required electrical conductivity. Nylon 12/carbon nanotubes composite material is frequently used in fuel line systems because of its chemical resistance to gasoline. Specific applications in automotive fuel line components can be quick connectors, filters, and o-rings for fuel connectors.

Figure 3.9 illustrates an automotive fuel line system that uses conductive carbon nanotubes composite materials (Rich 2002; Hyperion Catalysis). Another application area of carbon nanotubes composite materials is thermo plastic exterior fenders for in-line electrostatic painting (PT 2001). Electrostatic spray painting is used to apply the topcoat to minimize overspray and emissions of solvents to the environment, and to increase surface coating quality. Having a conductive plastic removes the need to spray a conductive primer before the topcoat. Moreover, these composite materials allow a high quality surface coating with a low loading of carbon nanotubes and maintain the resin's ductility so that the fender will exhibit ductility in a low temperature impact.

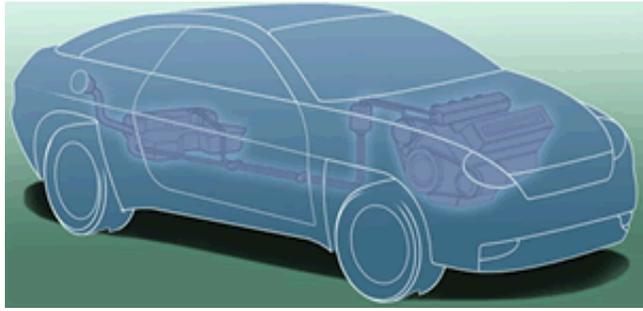


Figure 3.9 Fuel line systems that use conductive carbon nanotube composites.

Figure 3.10 shows the changes of volume resistance in a carbon nanotubes composite material, polycarbonate (PC) matrix. Percolation threshold is between 1 ~ 2 wt% in the well mixed sample. At 2 wt% loading the volume conductivity is within the range needed for electrostatic dissipative (ESD) applications (Collins 2004).

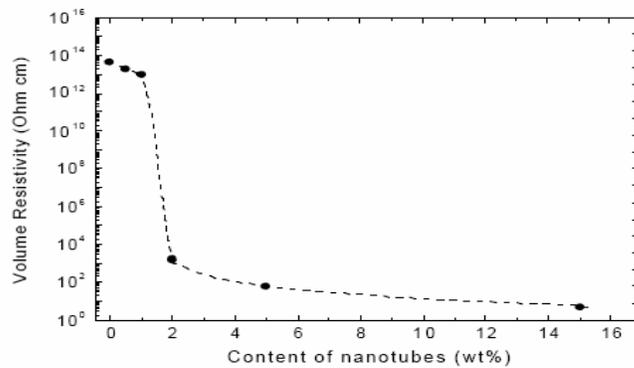


Figure 3.10 Change of volume resistivity with changes of carbon nanotube contents

3.4.1.3 Sporting goods

Carbon nanotube composite materials are used for sporting goods because of their lightweight and enhanced strength compared to conventional composite materials. Various products are available in the market such as tennis rackets, golf clubs, and bicycle frames. Figure 3.11 is a sporting goods product made from carbon nanotube composite material (Easton).



Figure 3.11 Baseball bat made out of carbon nanotubes composite material.

3.4.1.4 Other applications

The thermal and flammability properties of polypropylene/multi-walled carbon nanotubes composites show a significant reduction in the peak heat release rate (HRR) compared to the neat resin. When the content of multi-walled carbon nanotubes is 1 wt%, the reduction of HRR is greatest. Carbon nanotube composite materials form a uniform network-structured floccules layer covering the surface without any crack or gap. This network reflects incident radiation heat into the air and thus reduces heat transfer to matrix resin. As a result, the pyrolysis rate of the resin is decreased (Kashiwagi 2004).

Carbon nanotubes filled polycarbonate (PC), polyetherimide (PEI), and polyetheretherketone (PEEK) are used in the electronic industry because of their smooth and hard surface properties. Additionally, to avoid electro-static damage, wafer transportation trays and computer hard disk drives use conductive carbon nanotube nanocomposite materials (Collins 2004).

3.4.1.5 Manufacturers of carbon nanotube composite materials

Table 3.7 shows list of several carbon nanotube composite materials suppliers.

Supplier & Tradename	Matrix Resin	Nano-Filler	Target Market
Creanova (Vestamid)	Nylon 12	Nanotube	Electrically conductive
GE Plastics (Noryl GTX)	PPO*/Nylon	Nanotube	Automotive painted parts
Hyperion	PETG`, PBT**, PPS†, PC, PP	Nanotube	Electrically conductive
Zyvex (Kentera)	Epoxy	Nanotube	Sporting goods
RTP	Nylon 12, 6. PC	Nanotube	Electrically conductive

Table 3.7 Representative carbon nanotube composite materials suppliers (Peter 2005; PT 2001). *: Polyphenylene oxide, `: Polyethylene Terephthalate, **: Polybutylene terephthalate, †: polyphenylene sulfide

3.4.2. Electronic applications

3.4.2.1 Conductive film

Carbon nanotubes can be used to make transparent conductive films that are used for touch screens and electrodes in electronic display devices. It is potentially a replacement for expensive indium tin oxide (ITO) film used for this same purpose. Carbon nanotubes based transparent conductive film is flexible and compatible with polymer substrates. The film can be made at room temperature using inexpensive roll-to-roll manufacturing techniques. Also, this film can be used to reduce electrostatic discharge and particles problems in electronic manufacturing processes (Robertson 2004; Unidym).

Figure 3.12 a) shows a carbon nanotubes-based transparent conductive film. Another application of conductive carbon nanotube film is electromagnetic interference shielding. Data storage, aerospace, and aeronautical fields are the main application areas. Figure 3.12 b) shows conductive film based data storage device.



Figure 3.12 Applications of carbon nanotubes based conductive film. a) Transparent conductive film (Unidym), b) Data storage device (Iomega).

3.4.2.2 Cooling system

Due to its high thermal conductivity, carbon nanotube film can serve as a thermal interface material to manage thermal issues in high power electronics. Vertically aligned carbon nanotube arrays perform well as a thermal interface material, and are being considered for thermal management of integrated circuit (IC) systems (Wu 2006; Xu 2006). A nanotubes-on-chip assembly structure is proposed by Kordas et. al., whereby a carbon nano-film is formed on a Si substrate using CVD, and then followed with laser patterning. These patterned carbon nanotubes blocks are then mounted on the chip. A chip with a multi-walled carbon nanotubes cooling structure demonstrates 11% more powder dissipation compared to a conventional cooling system (Kordas 2007). Figure 3.13 illustrates the carbon nanotubes-on-chip structure and provides a sketch for a carbon nanotubes array structure for IC cooling.

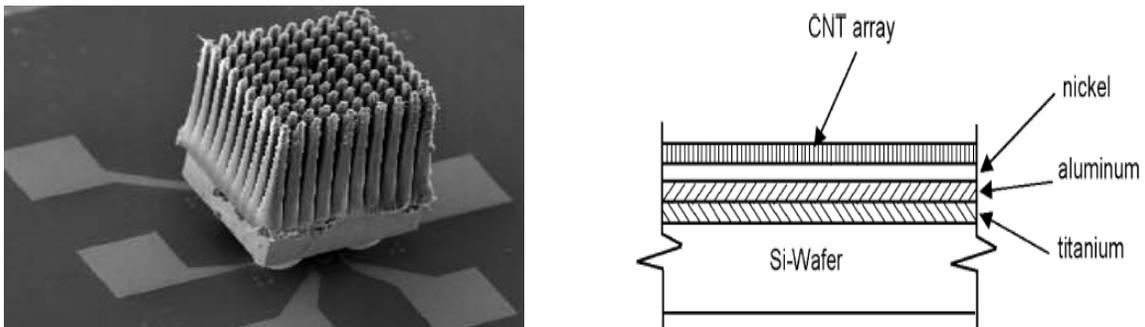


Figure 3.13 Carbon nanotubes-on-chip (Kordas 2007) and cooling structure using carbon nanotubes array (Xu 2006).

3.4.2.3 Field emission

The high aspect ratio of carbon nanotubes makes them ideal for field emission materials. Carbon nanotubes can substitute conventional silicon (Si) or tungsten (W) tips because carbon nanotubes are chemically and physically more stable, and can carry a large current density of 10^9 A/cm^2 (Robertson 2004). For example, carbon nanotubes can be used as electron guns for scanning/tunneling electron microscopy, X-rays generators, and cathodes in high power microwave amplifiers.

Another potentially major application for carbon nanotubes is as an electron emitter for flat panel display devices. Electrons from carbon nanotubes emitters are used to create an image on a screen of phosphor pixels. Carbon nanotube display has advantages over LCD or other displays in higher power efficiency and a wider operating temperature (Robertson 2004). Figure 3.14 shows an individual carbon nanotube emitter and full color display using carbon nanotube emitters.

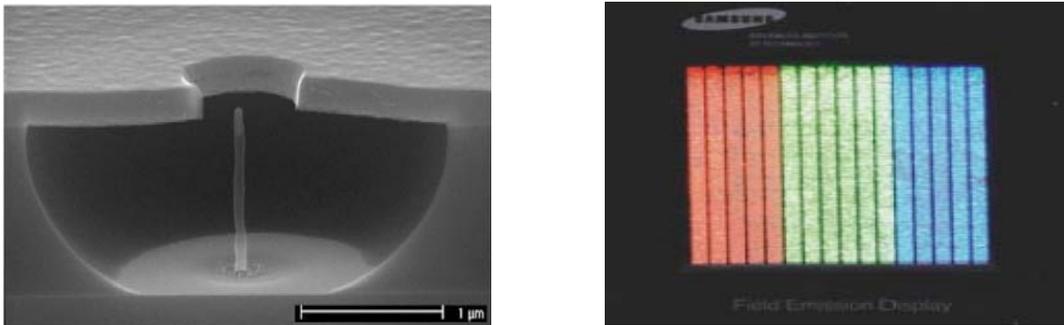


Figure 3.14 A single multi-walled carbon nanotube emitter grown by plasma enhanced CVD for field emission application (Robertson 2007) and color emitting image of carbon nanotube field emission display with red, green, and blue color (Choi 1999).

3.4.2.4 Field effect transistors

Carbon nanotubes are being considered in integrated circuits for the interconnection between field effect transistors and for the channel material in field effect transistors (Robertson 2007). Because the current density of carbon nanotubes is about 10^9 A/cm^2 (1000 times greater than copper), carbon nanotubes can replace the horizontal and vertical metal interconnects in transistors without degradation (Robertson 2004).

3.4.3 Energy applications

3.4.3.1 Batteries and capacitors

The large surface area and low resistivity of carbon nanotubes make them of great interest in electrochemistry. Carbon nanotubes have been used as electrode material in energy storage devices (e.g., batteries, capacitors) because of their large and controllable surface area. The energy density of a capacitor is proportional to the surface area per unit volume of the electrode. Single-walled carbon nanotubes have large surface area to volume ratio, $3000 \text{ m}^2/\text{g}$, as all their atoms are on the surface (Robertson 2004).

The energy storage systems that use carbon nanotubes as an electrode are reported by Pushparal et. al. (Pushparal 2007). Multi-walled carbon nanotubes grown by CVD on Si substrate embed into cellulose and form uniform film. This film can be rolled up, twisted, or bent to any curvature. Capacitors, batteries or hybrid energy storage devices can be made using these films. Figure 3.15 shows a schematic diagram of such storage device structures (modified from Kiebele 2007). Also, because of their light weight and conductivity, carbon nanotubes can be used as the charge collector and cathodes in very thin and light weight printable batteries.

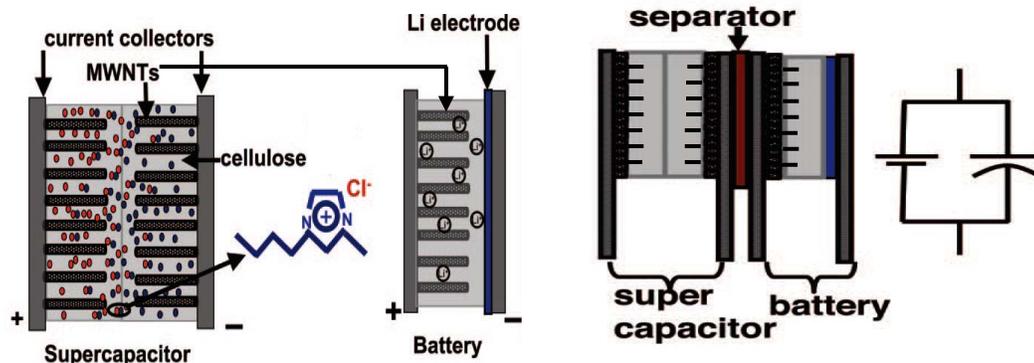


Figure 3.15 Schematic diagram of storage device: capacitor, battery, and hybrid structures.

A printable battery is made by solution based roll-to-roll ink printing processes at room temperature. Printable batteries have applications where portable, light-weight and disposable power is required such as portable electronics, wearable electronics, and radio frequency identified devices (RFIDs).

3.4.3.2 Solar cells

Carbon nanotube technology can improve the conversion efficiency in photovoltaic cells. As a transparent electrode material, carbon nanotubes are used in the flexible and efficient solar cells. Additionally, a polymer-composite material containing carbon nanotubes provides percolating channels for hole transport to the electrode.

Carbon nanotube networks have the potential to improve performance and are less expensive than competing ITO technology. The ability of carbon nanotubes to accept electrons and transfer them to a suitable electron acceptor makes them as good material in the charge transfer process. This electron-charging and discharging property of carbon nanotubes will play an important role in improving the performance of energy applications (Bjorklund 2007; Sholklapper 2007).

3.4.3 Ceramic matrix and metal matrix composite materials

3.4.3.1 Carbon nanotubes/ceramic composite materials

Incorporating carbon nanotubes into a ceramic matrix can improve both fracture toughness and hardness of materials. The mixed powders of carbon nanotubes and aluminum oxide (Al_2O_3), 300nm in average particle size, are ball-milled and then spark-plasma sintering is used under vacuum to make the composite material. Silicon oxide (SiO_2), vanadium oxide (V_2O_5) and Fe- Al_2O_3 are also used for ceramic matrix composite materials (Zhan 2003; Harris 2004). Figure 3.16 shows transmission electron microscopy (TEM) image of carbon nanotubes/ Al_2O_3 composite materials.

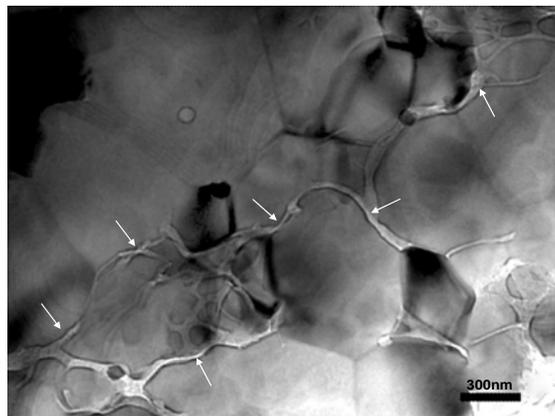


Figure 3.16 Transmission electron microscopy (TEM) image of carbon nanotubes/ Al_2O_3 composite materials. The arrows indicate the carbon nanotube phase (Zhan 2003).

3.4.3.2 Carbon nanotubes/metal composite materials

The carbon nanotubes/metal nanocomposite materials have very low density with high strength. The mechanical mixing of carbon nanotubes and metal powders, followed by hot pressing is used to make composites. For example, carbon nanotubes composites with titanium, aluminum, and magnesium can be used in aerospace industry. Also, a carbon nanotubes/nickel/phosphorus composite exhibits good wear resistance and low friction coefficient (Kuzumaki 2000; Harris 2004).

3.4.4 Other applications

3.4.4.1 Sensors in bio-health

Bio-sensors using carbon nanotubes can be categorized as aligned nanotube arrays or single-walled carbon nanotube field effect transistor (FET) electrodes. Carbon nanotube array sensors provide high speed analysis, analysis in resistive solutions, and analysis of very small volumes. FET sensors use semiconducting single-walled carbon nanotubes as the conducting channel.

The FET sensor is sensitive to various gases such as ammonia and can even detect a single molecule in air or liquid (Gruner 2006; Yun 2007). Figure 3.17 shows field effect transistor (FET) with carbon nanotube conducting channel (modified from Gruner 2006).

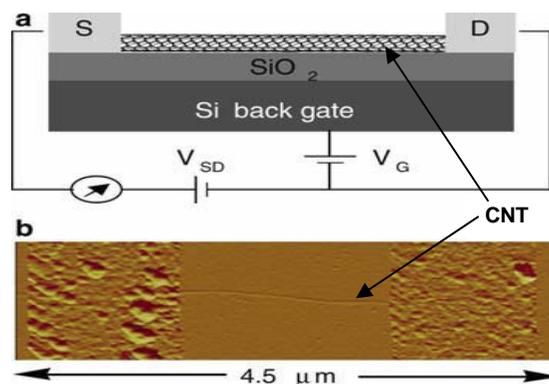


Figure 3.17 Field effect transistor with carbon nanotube conducting channel. a) cross-sectional view of system, b) AFM image of system surface.

3.4.4.2 Probe-tips

Carbon nanotubes can be used as the probe tip in atomic force microscopy (AFM) or scanning probe microscopy (SPM). Carbon nanotube probe tips can improve resolution compared to conventional Si or metal probe tips. Also, the high elasticity of carbon nanotubes

serves to prevent tip damage when contacting surfaces. Figure 3.18 shows one example of carbon nanotube tip used in an atomic force microscopy.

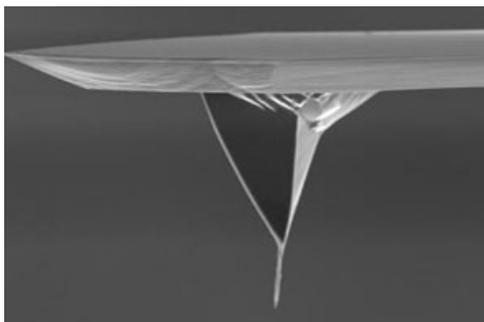


Figure 3.18 Carbon nanotube tip in AFM (Xintek)

3.5 Manufacturers of carbon nanotubes

Table 3.8 lists some of the domestic and overseas manufacturers of carbon nanotubes. The list is not comprehensive but representative of the industry.

1	Hyperion catalysis international (MA)	11	Arkema (France): MWCNT. 10tons/yr
2	Bayer MaterScience: 200 tons/yr (Germany)	12	Nanocyl (Belgium): 35 tons/yr
3	Ahwahnee Inc. (CA): China.	13	Carbon Nano-Materials Tech.(Korea)
4	Hanwha chemical (Korea)	14	Showa Denka (Japan): 100tons/yr in 2008
5	Raymor Industries, Inc. (Canada): 3.5 tons/yr. SWCNT	15	Carbon Nanotechnologies, Inc. (TX)
6	Vorbeck Materials Corp. (MD)	16	Thomas Swan & Company (UK).
7	Applied Sciences, Inc. (OH)	17	Helix materials solution (TX)
8	Nanostructured & Amorphous Materials, Inc. (NM)	18	Carbon solution (CA)
9	Cnano (CA): produced in China.	19	American element (CA): China.
10	Mitsui (Japan)		

Table 3.8 Representative list of carbon nanotubes manufacturers.

Production capacities vary with some companies producing more than hundreds of tons of carbon nanotubes per year. There are also many small companies that make small amounts of carbon nanotubes for research purposes. Some companies produce carbon nanotubes for their sole use only without selling to customers. Most companies listed make both single-walled and multi-walled carbon nanotubes.

IV. TITANIUM DIOXIDE (TiO₂) NANOMATERIALS

TiO₂ particles have long been used as a large band gap material because they are very stable and cheap compared to other materials. TiO₂ has been used as a white pigment from ancient time (Hashimoto 2005). TiO₂ is an essential ingredient in paints, inks, plastics, and rubber. The paint industry uses TiO₂ as a white pigment and is the largest consumer of TiO₂, consuming more than 50% of world TiO₂ production. The world wide market for TiO₂ pigment is about \$9 billion (CRISTAL; Altairnano; DuPont). However, these usages are for micrometer size TiO₂ particles. The overall U. S. market for TiO₂, including conventional and nanotechnology, is projected to \$2.2 billion in 2009 and \$2.3 billion by 2012 (Reuters). With recent developments in nanotechnology, nanosized TiO₂ particles have begun to receive widespread usage. The production capacity of TiO₂ nanoparticles is estimated 5,000 tons in 2008-10 (UNEP).

4.1 Crystal structures and properties of TiO₂ nanoparticles

4.1.1 Crystal Structure of TiO₂

There are three different crystal structures of TiO₂, each with different properties. These include anatase, rutile, and brookite. The anatase structure has 3.2 eV of band gap energy and absorbs ultraviolet radiation, $\lambda=388\text{nm}$ or shorter wavelength. The anatase structure is the most photoactive and has practical applications in water and air purification (Hoffmann 1995). The anatase structure exhibits higher overall photocatalytic activity due to difference in the position of the conduction band and has a stronger reducing power than that of the the other structures.

The rutile structure has a band gap of 3.0 eV and absorbs the ultraviolet rays as well as rays that are slightly closer to visible light. TiO₂ rutile structure is the most common white pigment in paint products due to its extremely high refractive index ($n=2.8$) (Gleiche 2006) and it can be used in UV protection products.

The third structure, brookite, absorbs wavelengths close to visible light. The brookite structure is not used in industrial applications. Figure 4.1 shows two crystal structures of TiO₂ material that are used in industrial applications. In TiO₂ crystal structure, Ti⁴⁺ ion is surrounded by an octahedron of six O²⁻ ions (Linsebigler 1995).

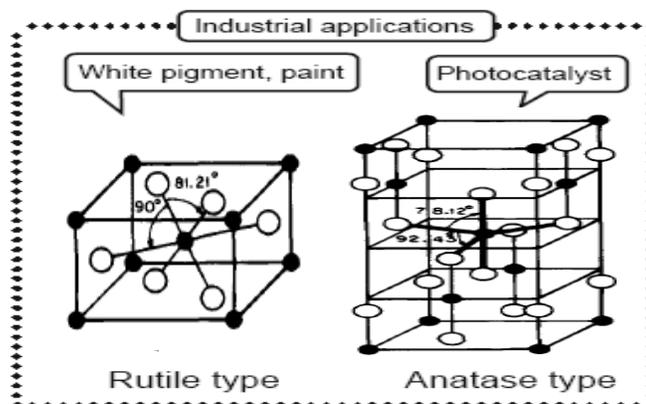


Figure 4.1 Crystal structures of TiO_2 , which are used in industrial applications. ●: titanium, O: oxygen (Linsebigler 1995).

4.1.2 Energy band structure of TiO_2

In TiO_2 , titanium atoms exist in the conduction band and oxygen atoms locate in the valence band (ThreeBond; Chen 2007). TiO_2 is a semiconductor and normally has an electronic band gap larger than 3.0 eV and absorbs light in the UV range. In semiconductors, electrons in the valence band can jump into the conduction band when external energy such as thermal or sunlight is applied. This phenomenon is called “excitation”. Figure 4.2 shows the relationship of excitation and recombination of carriers.

The excited state of a semiconductor is generally unstable and can easily break down. However, titanium dioxide remains excitation state longer than other materials when it is photoexcited. This is one of the properties that makes titanium dioxide an excellent photocatalyst. This stable state allows electrons and holes to react with other species before their recombination.

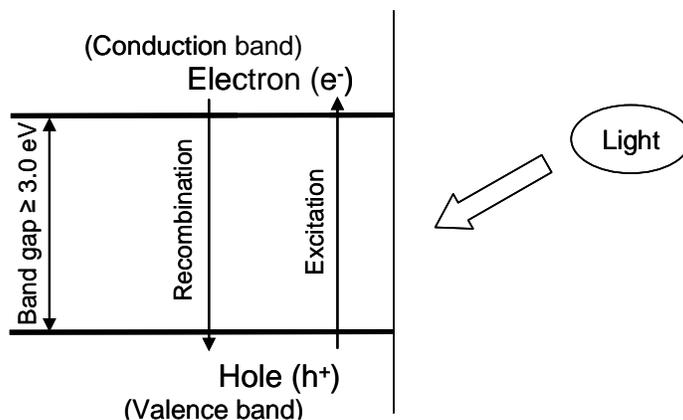


Figure 4.2 Electron band structure of TiO_2 (modified from ThreeBond).

4.1.3 Decomposing power of TiO₂

When TiO₂ absorbs light, electrons (e⁻) and holes (h⁺) are formed. In ordinary substances, e⁻ and h⁺ recombine quickly; however, in TiO₂ they recombine more slowly. This recombination property is a key element of TiO₂'s photocatalytic efficiency.

One of the notable features of TiO₂ is the strong oxidative decomposing power of positive holes (h⁺), which is greater than the reducing power of electrons excited to the conduction band. When water on the surface of the photocatalyst is oxidized by positive holes, hydroxyl radicals (•OH) are formed which have strong oxidative decomposing power. These hydroxyl radicals react with organic matter, which eventually decomposes, ultimately to carbon dioxide and water. Also, under certain conditions, organic compounds can react with directly with the positive holes, resulting in oxidative decomposition.

At the same time, the reduction of oxygen contained in the air occurs as a pairing reaction. This reduction reaction results in the generation of superoxide anions, (•O₂⁻). The superoxide anion attaches to the intermediate product in the oxidative reaction and elevates the oxidative decomposition reaction. The reduction of oxygen consumes electrons, reducing the rate of recombination with positive holes in the valence band. Reducing the recombination rate serves to enhance the overall oxidative decomposition reactions by positive holes. Figure 4.3 illustrates reactions of electron and hole during the decomposition of pollutants by TiO₂ photocatalytic function after photoexcitation.

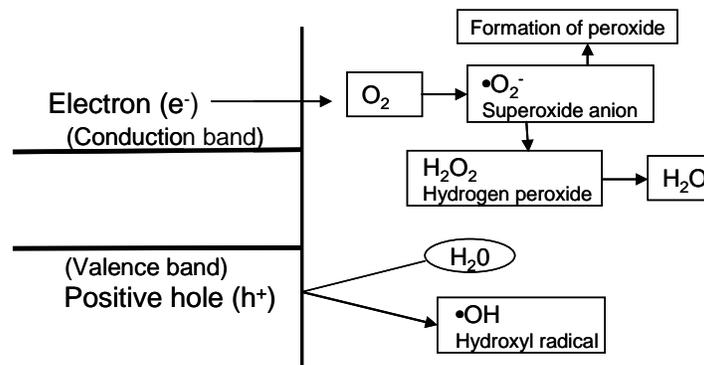
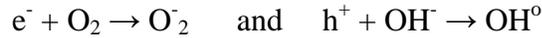


Figure 4.3 Reactions of electron and hole in photocatalytic process (modified from ThreeBond).

Sequence of photocatalytic reaction (photo decomposition) can be expressed as below.

1. Absorption of energy (photon) larger than band gap of TiO₂.
2. Formation of electron-hole pair by electron excitation.

3. Movement of charged potential to surface and formation of radicals.



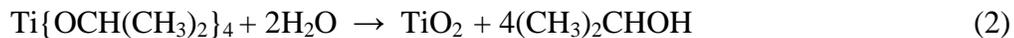
4. Radicals react with organic pollutants, oxidizing to CO₂, H₂O.

4.2 Fabrication methods for TiO₂ nanoparticles

Approximately more than half of world TiO₂ production is processed by the chloride process (using titanium tetrachloride) and DuPont is the largest supplier.

4.2.1 Sol-Gel process

TiO₂ nanoparticles are formed by titanium precursors, titanium alkoxide (Ti{OCH(CH₃)₂})₄). Titanium alkoxide (or Titanium tetraisopropoxide, TTIP (Ti{OCH(CH₃)₂})₄), is processed from titanium tetrachloride (TiCl₄) and alcohol. Size and shape of TiO₂ nanoparticles can be controlled by changing process conditions such as pH and shape controllers (amine, sodium oleate) (Sugimoto 2003). The process equations are expressed below and titanium dioxide is precipitated accordingly.



Another method for TiO₂ nanoparticles uses ammonia and titanium tetrachloride as starting materials (Ichinose 1996, 2000). In this process, titanium hydroxide (TiO(OH)₂) or titanium acid (H₂TiO₃) is precipitated by adding ammonia solution (NH₄OH) to TiCl₄ solution. To obtain pure TiO(OH)₂ requires washing with distilled water and centrifugation to remove the ammonium and chloride ions. Hydrogen peroxide solution is then added to get H₄TiO₄ (peroxotitanium acid). Finally, TiO₂ particles are formed by heating to over 100°C and holding at that temperature for 6 hrs. Figure 4.4 is a process flow schematic for TiO₂ particles formation.

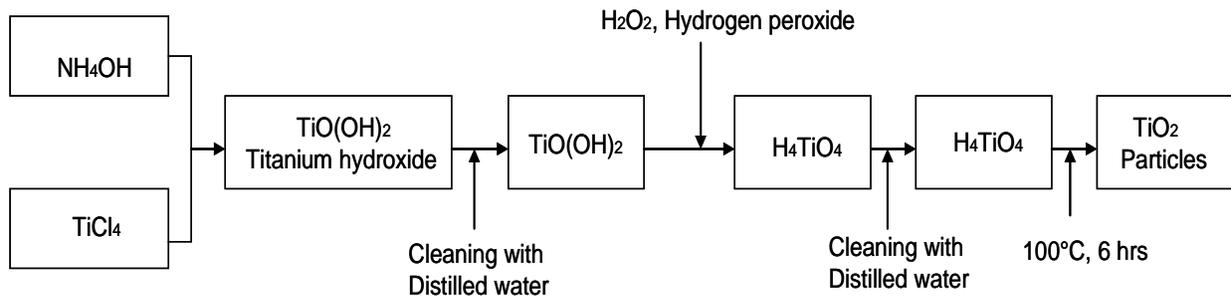
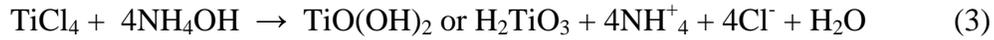


Figure 4.4 Process flow diagrams for formation of TiO₂ particles with NH₄ and TiCl₄.

The process equations are as follows:



4.2.2 Hydrolysis

TiO₂ nanoparticles can also be fabricated using the hydrolysis process, shown in Figure 4.5. TiO₂ particles fabricated by this method are amorphous and require calcination to convert to a high crystalline structure. Feed solution for fabrication of TiO₂ nanoparticle is a mixture of TiCl₄ and HCl. This mixture forms a titanium oxychloride solution (TiOCl₂ + H₂O), which is sprayed and evaporated on a hot plate to form dense amorphous TiO₂ thin films.

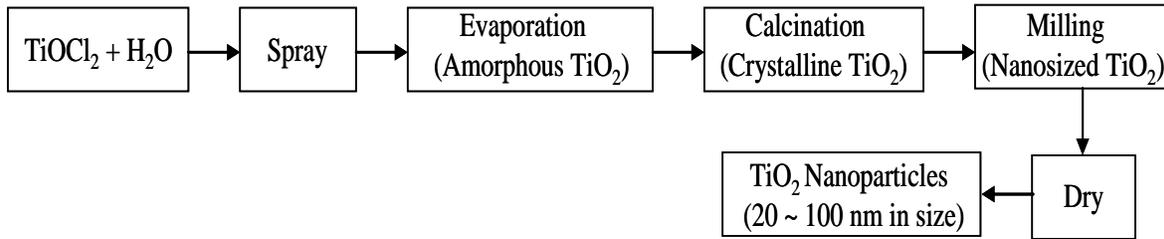


Figure 4.5 Process flow diagrams for fabrication of TiO₂ nanoparticles by hydrolysis.

The amorphous thin films are then calcinated to form a crystal structure. Particle size and structure can be controlled by changing calcination time, temperature, and additives such as phosphates to stabilize the anatase structure in TiO₂ particles. To produce the nanosized TiO₂ particles, the calcinated crystalline TiO₂ is milled. A wet milling with zirconia beads can be used and the milled slurry is dried to yield nanoparticles, 20 nm ~ 100 nm in diameter (Altairnano; Altairnano Tech. Report).

4.2.3 Other methods for fabrication of TiO₂ nanoparticles

TiO₂ nanoparticles can be obtained by a hydrothermal process using peptized precipitates of titanium precursors with water in an autoclave. This process is widely used in the ceramic industry (Chen 2007). Chemical vapor deposition or physical vapor deposition are used to deposit nanoparticles on a substrate. In chemical vapor deposition, Ti source materials are vaporized by a gas, introduced into the reaction chamber at above 500°C, and TiO₂

nanostructures are grown directly on the substrate. Pure Ti metal is used as the source material for physical vapor deposition. Thermal evaporation and sputtering are common physical vapor deposition processes. It is also possible to produce TiO₂ nanorods and nanowires by modifying CVD process conditions in the nanoparticle fabrication processes.

4.3 Applications of TiO₂ nanoparticles

TiO₂ nanoparticles have a diverse range of applications and can be used for ultraviolet (UV) protection, photocatalysts, photovoltaics, sensors, photochromics, water treatment to degrade chlorinated compounds, anti-bacterial agents for medical devices and food preparation, fungicides, and air purification/deodorizing.

4.3.1 Photocatalytic applications

For photocatalytic applications, the TiO₂ anatase structure is used because of its higher photocatalytic activity. Generally, the efficiency of a catalyst depends on its chemical reactivity, surface area, and temperature. When other conditions are held constant, surface reaction rates are faster with a large surface area and constant surface density. Thus the extremely large surface area of nanomaterials provides higher catalytic activity.

4.3.1.1 Self-cleaning using photocatalytic function

TiO₂ is one of the most efficient photocatalysts. The oxidizing power of illuminated TiO₂ even kills bacteria. Photocatalytic reaction results in formation of free radicals which are very effective in degrading organic matter. When exposed to ultraviolet light, the surface of TiO₂ shows highly hydrophilicity (photo-induced hydrophilicity) (Hashimoto 2005).

The photocatalytic reaction depends on the chemical properties and particles size of TiO₂. To improve the photocatalytic property, metal or non-metal ions such as Al³⁺, Fe³⁺, La³⁺, Be²⁺, nitrogen, sulfur, carbon, and fluorine are doped on TiO₂ nanomaterials. Doped ions increase degradation of various organic pollutants under UV and visible light (Chen 2007; Hoffmann 1995).

4.3.1.2 Products using TiO₂ photocatalytic property

Self cleaning products using the photocatalyst function and hydrophilic nature of TiO₂ nanomaterials are available in glass for buildings, exterior walls of buildings, interior tiles, roofing and tents, automobile mirrors, road materials, medical devices, deodorization, and food preparations. More than 40 companies employ TiO₂ photocatalyst technology¹⁴ (TOTO).

Different coating processes are available to apply TiO₂ nanomaterials onto the surface of glasses or tiles. For example, Pilkington ActivTM uses chemical vapor deposition to coat on the surface of glasses with a 40 nm thick TiO₂ film at 600°C (Gould 2003). A TiO₂ film can also be coated using a dip-coating process that dips the substrate into the solution of TiO₂ nanoparticles, which is dried (Ichinose 1996; Ichinose 2000). Another common method is spray coating. TiO₂ nanoparticles are sprayed on surface of tiles or glasses and then heated to 500°C ~ 600°C to improve adhesion (Green Millennium). These different coating technologies provide clear, hard coatings for glass, plastics, metals, and ceramics. Figure 4.6 is a schematic picture for spray coating of TiO₂ material on tiles.

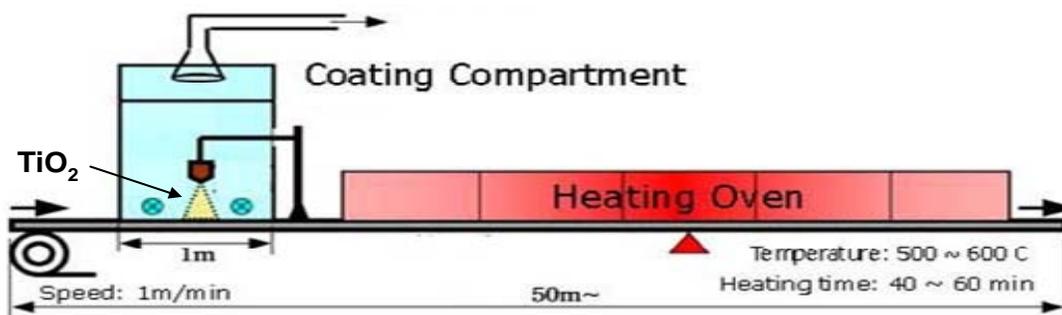


Figure 4.6 Spray coating process for TiO₂ photocatalyst on tiles (modified from Green Millennium).

Figure 4.7 shows some examples of commercially available self cleaning products. Self cleaning products for exterior walls and windows of buildings rely on ultraviolet light and rain water to promote photocatalytic properties. Automobile mirrors and road construction materials provide anti-fogging and good visibility, while roofing and tents materials block ultraviolet rays and prevent soiling. Self sanitizing and anti-bacterial coating are used on interior tiles and on the surface of computer peripherals such as mouse and key board (Iogear).

¹⁴ Pilkington, UK; Saint-Gobain Glass, FRA; TOTO, JPN; Taiyo Kogyo, JPN; PPG industry, USA; Deutsche steinzeug cremer & breuer, GER etc.

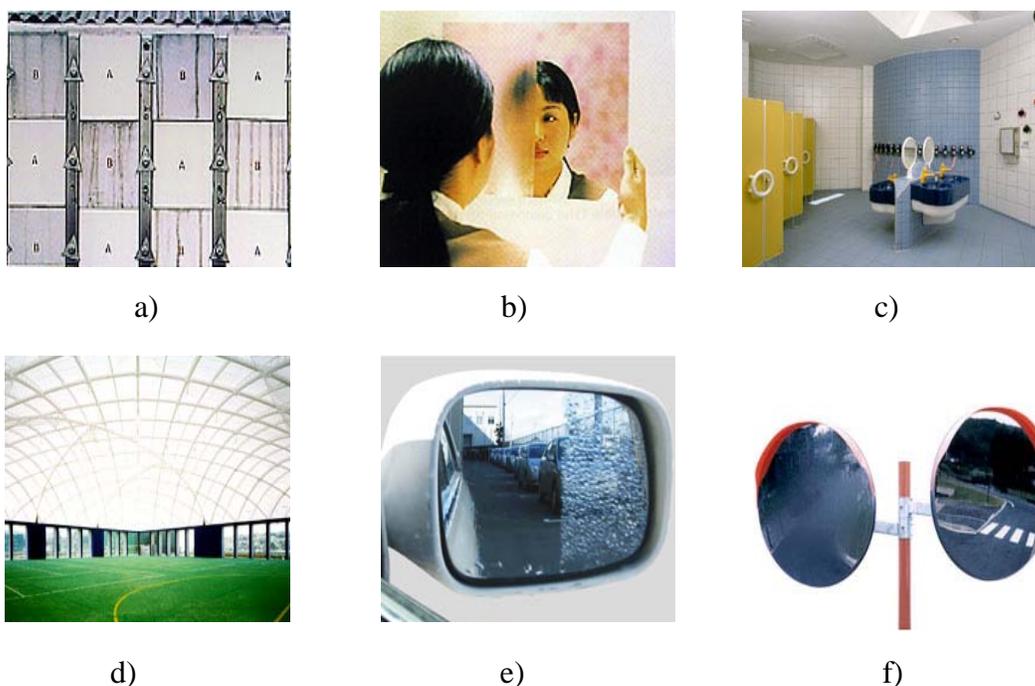


Figure 4.7 Examples of self cleaning products available in market (Fujishima 1999; TOTO). a) exterior building wall; A: tiles TiO_2 coated, B: ordinary tiles, b) anti-fog coating, c) interior tiles, d) tent and roofing, e) automobile mirror, f) road materials.

4.3.1.3 Personal care (Sun screen)

Rutile structure TiO_2 nanoparticles are used in sunscreens to absorb harmful ultraviolet (UV) radiation that damages the skin. Many types of sunscreen products using TiO_2 nanoparticles are currently available in the market. Larger than the nanoscale, TiO_2 particles scatter visible light radiation which makes them a very good white pigment in paint, but a problem in sunscreens. TiO_2 nanoparticles less than 50 nm in diameter which is transparent to visible light are now commercially available. These nanoparticles have large band gaps which cause them to lose their ability to scatter visible light, making them transparent. While the use of TiO_2 nanoparticles makes sunscreens transparent, the particles still absorb the higher-energy (shorter wavelength) ultraviolet radiation (Rogers 2008). When using TiO_2 for UV protection in sunscreen the rutile structure is more stable due to its lower photocatalytic activity (Gleiche 2006).

4.3.1.4 Photocatalytic water splitting

Photocatalytic splitting of water into H_2 and O_2 using TiO_2 nanomaterials is a potential sustainable energy source. When TiO_2 absorbs light with greater energy than the band gap,

electrons and holes are generated (see Figure 4.2). The photogenerated electrons and holes cause oxidation/reduction reactions. Water molecules are reduced by the electrons to form H_2 and oxidized by the holes to form O_2 . In this reaction, TiO_2 nanomaterial is used as the electrode. Doped TiO_2 or dye sensitized TiO_2 can be used to improve the reaction efficiency. Figure 4.8 illustrates water splitting system that uses doped TiO_2 nanomaterial as an electrode (Takabayashi 2004).

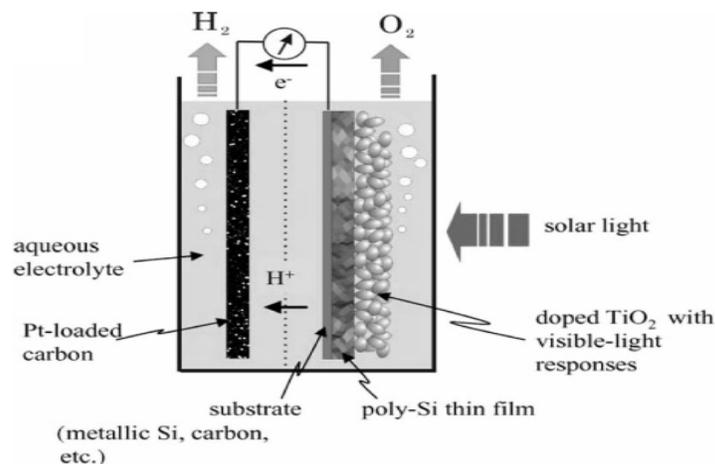


Figure 4.8 Composite solar water splitting system with doped TiO_2 semiconductor electrode.

4.3.2 Photovoltaic applications (Solar cells)

Solar cells are generally constructed using two electrodes with a semiconductor layer(s) between them. TiO_2 nanoparticles can be transparent and function in solar cells as the electrons acceptor. In organic solar cells, solar radiation photoexcites the organic semiconductor layer which then emits electrons. These emitted electrons transfer to the semiconductor TiO_2 nanomaterials. To increase solar cell efficiency a patterned TiO_2 thin film containing numerous pores, a few nm in diameter, can be used. The organic polymer is melt-infiltrated into the pores by spinning and heating to form a TiO_2 /polymer structure (Bjorklund 2007).

TiO_2 nanoparticles can also be used in dye-sensitized solar cells. Like organic solar cells, TiO_2 nanoparticles act as electron acceptor. Photo excitation of the dye emits electrons which transfer to the TiO_2 nanoparticles and are then conducted to an outer circuit to drive a load. To improve efficiency, a core/shell structure (porous TiO_2 core/metal oxides shell; Al_2O_3 , MgO , etc)

can be used (Grätzel 2004). Figure 4.9 shows schematic diagrams of organic and dye-sensitized solar cell structures.

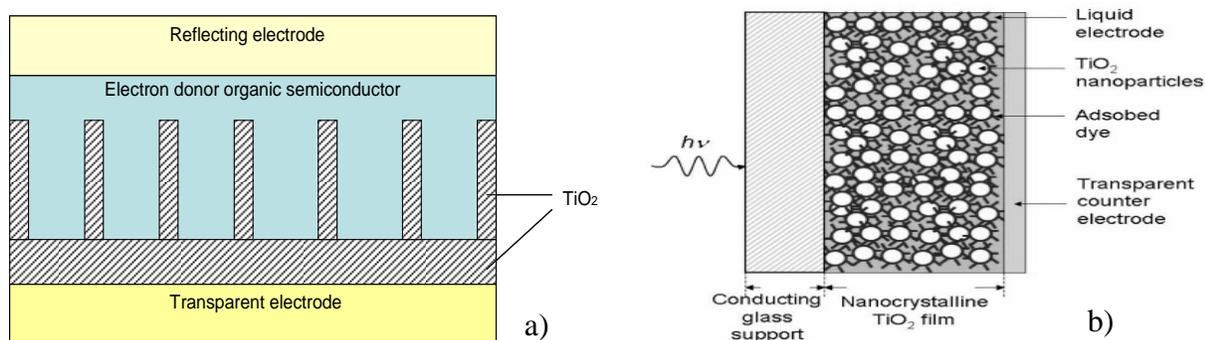


Figure 4.9 Schematic of solar cell structures. a) organic, b) dye sensitized solar cell.

4.3.3 Other applications

Other applications of the TiO_2 anatase structure using the photocatalytic function are water and wastewater treatment and disinfection (Hoffmann 1995), air purifier/sanitizer/odor remover, and self cleaning hot tub. TiO_2 nanomaterials also have application as sensors. For example, sensors based on TiO_2 nanoparticles are being developed for humidity, CO, methanol, ethanol, and oxygen (Chen 2007).

For energy storage, hydrogen could be stored between layers in the walls of TiO_2 nanotubes. TiO_2 nanotubes could store up to approximately 2 wt% of H_2 at room temperature at 6MPa, and 75% of H_2 could be released at ambient conditions (Lim 2005). The rate of hydrogen uptake increases with temperature (Bavykin 2005).

TiO_2 nanomaterials have been widely explored as electrodes in electrochromic¹⁵ windows and displays (Bonhote 1999). Also, TiO_2 nanoparticles can be used as an electron pass in lithium ion batteries, as the dielectric layer in electronics, and as a thermal barrier coating in machinery. TiO_2 nanoparticles also have potential application in batteries for electric cars. Batteries made out of TiO_2 and lithium, are expected to be commercialized in the near future (Phoenix MC).

¹⁵ Electrochromic window: window that can be darkened or lightened electronically by reduction/oxidation reaction when power is applied.

SUMMARY

More than 20% of the micro- and nanotech companies based in the United States are located in California, making the state a leader in nanotechnology¹⁶. A total of 226 companies in California were found to be involved with nanotechnology. The largest nanotechnology industrial sector in California is the materials industry with 69 companies located in California. Other major industrial sectors utilizing nanotechnology are those involving tools and instruments, electronics, bio-health, and energy. The number of California-located companies in each of these sectors ranged from 39 to 15. Additionally, there are 29 research institutes including universities, private research centers, non-profit organizations, and government research centers in California that conduct nanotechnology-related research. Having been a leader and center for the high tech industry, California has an excellent infrastructure in place and the potential for nanotechnology development is great. Many of California's nanotech companies are small businesses that have limited funding. Given limited resources, a concern facing these small businesses is the unknown public health and environmental impacts of nanomaterials, as well as the health and safety of the workers who handle these materials in the research and development, and manufacturing environments.

The two most prominent types of nanotechnology identified in California were carbon nanotubes (CNTs) and titanium dioxide (TiO₂). There are ten companies directly or indirectly involved with carbon nanotubes in California, one of which is at the R&D stage. Only one of the 10 companies identified actually makes carbon nanotubes commercially within California. All of these companies have a relatively short history, and most were established solely for newly found applications of carbon nanotubes. However, only a company's headquarters or research facility is located in California, while most manufacturing facilities are located outside of California, in other states or overseas.

Chemical vapor deposition is primary method used to manufacture carbon nanotubes, which are typically shipped in a powder form. Carbon nanotubes can also be produced using the arc discharge or laser vaporization methods. Eight of the ten companies are focused on manufacturing carbon nanotubes as a final product, while two companies use carbon nanotubes as raw material in manufacture of their products. Six of the companies manufacture other

¹⁶ Academics, government, and private research centers.

nanomaterials in addition to carbon nanotubes. Five of the companies produce both single and multi-walled carbon nanotubes, while the other companies produce either only single-walled or multi-walled carbon nanotubes.

No companies were found to make TiO₂ nanoparticles within California. California-based companies involved with TiO₂ nanotechnology have only a marketing function or are focused on research related to TiO₂ applications, and not manufacturing. TiO₂ nanoparticles are generally produced as a powder. While there are companies that distribute TiO₂ nanoparticles in California, all known manufacturing facilities are located outside California. Similar to carbon nanotubes, the technology is relatively new and the involved companies have a short history.

Carbon nanotubes have many applications ranging from plastic composites to atomic force microscopy (AFM) tips. Carbon nanotubes are used to enhance electrical conductivity and thermal property in plastic polymer composite materials. The higher aspect ratio of carbon nanotubes (1000:1) allows equivalent conductivity at lower loading compared to conventional conductive filler such as carbon black or carbon fiber. Carbon nanotubes filled conductive polymer composite materials are being used in several automotive parts, such as fuel line system parts and thermo plastic exterior fenders for in-line electrostatic painting. Carbon nanotube composite materials are used for sporting goods because of their lightweight and enhanced strength compared to conventional composite materials. Various products are available in market such as tennis rackets, golf clubs, bicycle frames, and yacht parts.

Carbon nanotubes can be used to make transparent conductive films for use in touch screens and electrodes in electronic display devices. Another application of conductive film is for electromagnetic interference shielding. The high thermal conductivity of carbon nanotube film is considered as a thermal interface material to manage heat buildup in high power electronics. Another great potential application for carbon nanotubes is as an electron emitter for a flat panel display device. Carbon nanotubes are also used in flexible solar cells, batteries and capacitors, probe-tips, and sensors in bio-health.

TiO₂ nanoparticles have a diverse range of applications and can be used for ultraviolet (UV) protection, photocatalysts, photovoltaics, sensors, photochromics, water treatment to degrade chlorinated compounds, anti-bacterial agents for medical devices and food preparation surfaces,

fungicides, and air purification/deodorizing products. The chloride process using TiCl_4 as the raw material is the primary method for producing TiO_2 nanoparticles.

Anatase structure TiO_2 nanoparticles have major application as a photocatalyst. Photocatalytic reactions form free radicals which can effectively degrade organic matter. Self cleaning products using the photocatalytic function and hydrophilic nature of TiO_2 nanomaterials are available in glass for buildings, exterior walls of buildings, interior tiles, roofing and tents, automobile mirrors, road materials, medical devices, deodorization, and food preparations. Other potential applications include solar cells, hydrogen production from water, and air, water and wastewater treatment. Rutile structure TiO_2 nanoparticles are used in sunscreens to absorb harmful, skin-damaging ultraviolet (UV) radiation. Many types of sunscreen products using TiO_2 nanoparticles are currently available in the market.

REFERENCES

- Blue Ribbon Task Force on Nanotechnology. Thinking big about thinking small: An action agenda for California. Dec. 2005.
- Small Times. "State Ranking Part Six: The all-category summary". July 2007.
- Collins, P. et al. "Carbon nanotubes: a high performance conductive additive". Materials Integrity Management Symposium. Boston, USA. June 6-9. 2004.
- Eston Sports. <http://www.eastonsports.com/> (Accessed on 03/2008)
- Gilman, J. et al. "Flammability of polymer clay nanocomposites consortium: Final report". U.S. Dept. of Commerce. 2003.
- Hyperion Catalysis, Inc. www.fibrils.com/automotive2.htm (Accessed on 03/2008).
- Jarus, D. et al. "Polyolefin nanocomposites in TPOs". TPOs in Automotive. Switzerland. June 21-23, 2005.
- Kashiwagi, T. et al. "Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites". Polymer. 45. 2004. 4227-4239.
- Lan, T. et al. "Application of Nanomer in nanocomposites: from concept to reality". Nanocomposites 2001. USA. June 25-27, 2001.
- Nanocor. <http://www.nanocor.com/> (Accessed on 03/2008).
- Naturalnano, Inc. <http://www.naturalnano.com/> (Accessed on 03/2008).
- Plastic Technology (PT), "Chasing Nanocomposites". Nov. 2004.
- Yang, C.M. et al. "Effect of purification on pore structured of HipCO single-walled carbon nanotube aggregates". Nano Letters. Vol. 2, No.4. 2002. 385-388.
- Plastic Technology (PT), "Nanocomposites Broaden Roles in Automotives, Barrier Packaging". Oct. 2001.
- Case Western Reserve University (CWRU). The web course of nanotechnology: Nanopedia. <http://nanopedia.case.edu/NWPPage.php?page=home> (Accessed on 10/2008).
- Plastic Technology (PT), "Nanocomposites: A little goes a long way". June. 1999.
- Plastic Technology (PT), "Nanocomposites". May. 1997.

Rich, A. et al. "Nanotubes for conductive plastics move to the next performance level". Society of Automotive Engineer. Paper No. 2002-01-1037.

Vaia, A.R. et al. "Framework for nanocomposites". Materialstoday Nov. 2004. 32-37.

Yoon, P.J. et al. "Effects of Nanoclay Structure on the Mechanical Properties of EPDM". Fall 170th Technical Meeting of the Rubber Division, American Chemical Society. Cincinnati, OH. Oct. 10-12, 2006.

Saito, Y. et al. "Field Emission from carbon nanotubes and its application to electron sources". Carbon. 38. 2000. 169-182.

Grobert, N. "Carbon nanotubes-becoming clean". Materialstoday. Vol. 10. No. 1-2. 2007. 28-35.

Ando, Y. et al. "Growing carbon nanotubes". Materialstoday. Oct. 2004. 22-29.

McCann, J.T. et al. "Carbon nanotubes by electropinning with a polyelectrolyte and vapor deposition polymerization". Nano letters. Vol. 7. No. 8. 2007. 2470-2474.

Robertson, J. "Realistic applications of CNTs". Materialstoday. Oct. 2004. 46-52.

Robertson, J. "Growth of nanotubes for electronics". Materialstoday. Vol. 10. No. 1-2. 2007. 36-43.

Wu, Q.B. et al. "Template based synthesis of carbon nanofibers and their field emission". Surface Interface and Analysis. Vol. 36. Issue 5-6. 2004. 493-496.

Ando, Y. "The preparation of carbon nanotubes". Fullerene Science and technology. Vol. 2. Iss. 2. 1994. 173-180.

Tai, Y. et al. "Identification of compounds produced through contact arc vaporization of graphite under CH₄ ambience". Chem. Phys. Lett. Vol. 224. Iss. 1-2. 1994. 118-122.

Bacsa, W.S. "Carbon nanotubes fundamentals and applications". 2007 Nano Science and Technology Institute. Nano industrial impact workshop Course Notes. Santa Clara, CA. May 2007.

Kordas, K. et al. "Chip cooling with integrated carbon nanotube micro-fin architectures". Appl. Phys. Letter. 90. 2007. 123105.

Wu, Y. et al. "Thermal properties of carbon nanotube array used for integrated circuit cooling". Journal of applied physics. 100. 2006. 074302.

Iomega corp. www.iomega.com (Accessed on 05/2008).

Xu, J. et al. "Enhancement of thermal interface materials with carbon nanotubes arrays". *Int. J. of Heat and Mass Transfer*. Vol. 6. 2006. 1658-1666.

Choi, W.B. et al. "Fully sealed, high-brightness carbon nanotube filed emission display". *Applied Physics Letters*. Vol. 75. No. 20. 1999. 3219-3131.

Pushparaj, V.L. et al. "Flexible energy storage devices based on nanocomposite paper". *PNAS*. Vol. 104, No. 34. 2007. 13574-13577.

Kiebele, A. et al. "Carbon nanotube based battery architecture". *Applied Physics Letters*. 91. 2007. 144104.

Zyvx performance materials. www.zyvespro.com (Accessed on 11/2007).

Dong, L. et al. "Carbon nanotubes for nanorobotics". *Materialstoday*. Vol. 2. No. 2. 2007. 12-21.

Bjorklund, G.C. et al. "Organic Thin film solar cell research conducted at Stanford University". *Photonics*. November. 2007. 70-76.

Sholklapper, T.Z. et al. "Nanostructured Solid Oxide Fuel Cell Electrodes". *Nanoletters*. Vol.7. No. 7. 2007. 2136 ~ 2141.

Gruner, G. "Carbon nanotube transistors for biosensing application". *Anal. Bioanal. Chem.* 384. 2006. 322-335.

Yun, Y. et al. "Nanotube electrodes and biosensing". *Materialstoday*. Vol.2. No. 6. 2007. 30-37.

Xintek, Inc. www.xintek.com (Accessed on 07/2008).

Sugimoto, T. et al. "Synthesis of uniform anatase TiO₂ nanoparticles by gel-sol method 4. Shape control". *J. of colloid interface Sic.* 2003. 259.53.

Ichinose, H. et al. "Properties of peroxotitanium acid solution acid solution and peroxommodified anatase sol derived from peroxotitanium hydrate". *J. of Sol-gel Sci. and Tech.* 22. 33-40. 2000.

CRISTAL. <http://www.cristalarabia.com> (Accessed on 05/2008)

Meyyappan, M. "Carbon nanotubes: Science and application". CRC Press. 2004.

Fujishima, A. et al. "TiO₂ photocatalysis fundamentals and applications". BKC publisher. May 1999. Tokyo, Japan.

Takabayashi, S. et al. "A nano-modified Si/TiO₂ composite electrode for efficient solar water splitting". *Photochem. Photobiol. A: Chem.* 166 (1-3), 2004, 107-113.

Altairnano. <http://www.altairnano.com> (Accessed on 05/2008)

UNEP GEP YEAR BOOK 2007. Emerging challenges: Nanotechnology and the environment.

Altairnano Technical report. "A new process for the production of nano-sized TiO₂ and other ceramic oxides by spray hydrolysis".

Lim, S.H. et al. "Room-Temperature Hydrogen Uptake by TiO₂ Nanotubes". Inorganic chemistry. 44 (12), 2005. 4124-4126.

DuPont. "Nanomaterial risk assessment worksheet DuPont light stabilizer". June. 2007.

Chen, X. et al. "Titanium dioxide nanomaterials: Synthesis, properties, modification, and applications". Chemical Review. 2007. 107(7). 2891-2959.

ThreeBond Technical News. "Titanium Dioxide Photocatalyst". January 1, 2004.

Ichinose, H. et al. "Properties of Anatase films for photocatalyst from peroxotitanic acid solution and peroxy-modified Anatase sol". J. of ceramic society of JPN. 104 (10). 1996. 914-917.

TOTO, Inc. <http://www.toto.co.jp> (Accessed on 05/2008)

Gleiche, M. et al. "Nanotechnology in consumer products". Nanoforum report. Oct. 2006. <http://www.nanoforum.org>

Gould, P. "Smart, clean surfaces". Materialstoday. Nov. 2003. 44-48.

Rogers, B. et al. "Shedding light on nanophotonics". Smalltimes. Jan/Feb. 2008. 22-24.

Iogear, Inc. <http://www.iogear.com/product/GME227RW6/> (Accessed on 05/2008)

Grätzel, M. "Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells". J. Photochem. Photobiol. A: Chem. 164. 1-3. 2004. 3-14.

Linsebigler, A. L. et al. "Photocatalysis on TiO₂ surface: principles, mechanisms, and selected results". Chemical Review. 95.1995. 735-758.

Campus, F. et al. "Electrochromic devices based on surface-modified nanocrystalline TiO₂ thin-film electrodes". Solar Energy Materials and Solar Cells. Vol. 56, No. 3, 1999. 281-297.

Hoffmann, M. R. et al. "Environmental application of semiconductor photocatalysis". Chemical review. 1995. 95. 69-96.

Green Millennium, Inc. <http://www.greenmillennium.com/gmiapplications.htm> (Accessed on 05/2008).

Phoenix Motorcars (MC). <http://www.phoenixmotorcars.com/> (Accessed on 07/2008).

Reuters. "Titanium dioxide market will rebound in 2009". June. 30. 2009.
Cheap tubes, Inc. www.cheaptubes.com (Accessed on 11/2008)

Begtrup, G.E. et al. "Extreme thermal stability of carbon nanotubes". Phys. Stst. Sol. (b) 2007. 244. No. 11. 3960-3963.

Kim Y.A. et al. "Thermal stability and structural changes of double walled carbon nanotubes by heat treatment". Chemical physics letters. 398. 2004. 87-92.

Hone, J. "Carbon nanotubes: Thermal properties". Dekker encyclopedia of Nanoscience and nanotechnology. 2004. Marcel Dekker, Inc. 603-610.

Ebbesen, T. et al. "Purification of nanotubes". Nature. 1994. 367. 519-

Montoro, L.A. et al. "A multi-step treatment to effective purification of single-walled carbon nanotubes". Carbon. 44. 2006. 3292-3301.

Shanov, V. et al. "Synthesis and characterization of carbon nanotube materials (Review)". J. of the Univ. of Chem. Tech. and Metal. 41. 4. 2006. 377-390.

Zheng, B. et al. "CVD synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst". Applied Physics A. 74. 2002. 345-348.

Harris, P. J. F. "Carbon nanotube composites". Int. Mat. Rev. 2004. Vol. 49. No. 1. 31-43.

Zhan, G.D. et al. "Single-wall carbon nanotubes as attractive toughening agents in alumina-based nanocomposites". Nature materials. Vol. 2. 2003. 38-42.

Hashimoto, K. et al. "TiO₂ photocatalysts: A historical overview and future prospects". Jap. J. of Appl. Phys. Vol. 44. No. 12. 2005. 8269-8285.

Bonhote, P. et al. "Novel electrochromic devices based on complementary nanocrystalline TiO₂ and WO₃ thin films". Thin solid films. 1999. Vol. 350. Issue 1-2. 269-275.

GLOSSARY

ABS: Acrylonitrile butadiene styrene
AC: Alternating current
AFM: Atomic force microscopy
Ag: Silver
Al: Aluminum
Al₂O₃: Aluminum oxide
Ar: Argon
Au: Gold
B: Boron
Be: Beryllium
C: Carbon
Cal/EPA: California Environmental Protection Agency
CeO₂: Cerium oxide
CH₄: Methane
C₂H₂: Acetylene
C₂H₄: Ethylene
CNT: Carbon nanotube
CO: Carbon monoxide
Co: Cobalt
CO₂: Carbon dioxide
Cu: Copper
CVD: Chemical vapor deposition
DC: Direct current
DWCNT: Double walled carbon nanotube
e⁻: Electron
eV: Electron volt
ESD: Electrostatic dissipative
Fe: Iron
FET: Field effect transistor
H₂: Hydrogen
HCl: Hydrochloric acid
He: Helium
HF: Hydrofluoric acid
HipCO: High pressure carbon monoxide
H₂O: Water
H₂O₂: Hydrogen peroxide
HRR: Heat release rate
h⁺: Hole
IC: Integrated circuit
ITO: Indium tin oxide
K: Absolute temperature
La: Lanthanum
LCD: Liquid crystal display
MWCNTs: Multi-walled carbon nanotube
MgO: Magnesium oxide

Mo: Molybdenum
 N: Nitrogen
 Na: Sodium
 NH₃: Ammonia
 NH₄OH: Ammonia solution
 Ni: Nickel
 nm: Nanometer
 O₂: Oxygen
 •O⁻: Oxide anion
 •OH: Hydroxyl radical
 Pa: Pascal
 PBT: Polybutylene terephthalate
 PC: Polycarbonate
 PC/ABS: Polycarbonate/Acrylonitrile butadiene styrene
 PEEK: Polyetheretherketone
 PEI: Polyetherimide
 PETG: Polyethylene Terephthalate
 PP: Polypropylene
 PPO: Polyphenylene oxide
 PPS: polyphenylene sulfide
 Pt: Platinum
 PVP: Polyvinylpyrrolidone
 QD: Quantum dot
 Rh: Rhodium
 S: Sulfur
 SDS: sodium dodecyl sulphate
 Si: Silicon
 SPM: Scanning probe microscopy
 SWCNT: Single-walled carbon nanotube
 Ti: Titanium
 TiCl₄: Titanium tetrachloride
 TiO₂: Titanium dioxide
 TiO(OH)₂: Titanium hydroxide
 TiOCl₂: Titanium oxychloride
 H₂TiO₃: Titanium acid
 TTIP: Titanium tetraisopropoxide (Ti{OCH(CH₃)₂}₄)
 UV: Ultraviolet
 V: Volt
 V₂O₅: Vanadium oxide
 W: Tungsten
 W: Watt
 Wt%: Weight percent
 Y: Yttrium
 YAG (Y₃Al₅O₁₂): Yttrium aluminum garnet
 ZnO: Zinc oxide
 ZrO₂: Zirconium oxide

APPENDIX

Appendix I: Directory of California Nanotechnology Companies
(Exclude venture capital, legal, and consulting companies)

1. Materials industry

	Name	Location	Products	Web site address
1	3D systems	Valencia	Composite mater.	http://www.3dsystems.com
2	Accelergy Corporation	Palo Alto	Catalyst	http://www.accelergy.com/
3	Advanced Thin Film, Inc	Santa Fe Spring	Thin Film	http://www.atfilminc.com/index.html
4	Ahwahnee, Inc	San Jose	CNTs	http://www.ahwahneetech.com/
5	Alpha Environmental	Los Angeles	TiO ₂	http://www.alpha-environmental.com
6	American Elements	Los Angeles	CNTs, TiO ₂	http://www.americanelements.com/
7	Apex Nanomaterials	San Diego	SWCNTs	http://www.apexnanomaterials.com/
8	Applied Microstructures, Inc	San Jose	Deposition system	http://www.appliedmst.com/
9	Atomate corporation	Santa Barbara	CVD system	http://www.atomate.com/
10	Behr Process corporation	Santa Ana	Paint (TiO ₂ ?)	http://www.behr.com
11	Berkeley advanced biomaterials	San Leandro	Nanoparticle	http://www.hydroxyapatite.com/
12	Beyond Skin Science, LLC	Corona	Skin Care	http://www.beyondskinscience.com/
13	BluemoonGoods	San Jose	Ag particles	http://www.bluemoongoods.com/
14	Callaway Golf	Carlsbad	Composite mater.	http://www.callawaygolg.com
15	Cambrios technology	Mountain view	Trans. electrode	http://www.cambrios.com/
16	Carbon Solutions	Riverside	SWCNTs	http://www.carbonsolution.com/
17	Catalytic Solution, Inc	Oxnard	Fuel catalyts	http://www.catalyticsolutions.com/
18	Catalyx Nanotech	Anaheim	Carbon nanofiber	http://www.catalyxnano.com
19	Chevron Corp.	San Ramon	Diamond	www.chevron.com
20	Cnano	Menlo Park	CNT	http://www.cnanotechnology.com
21	CV nanotechnology	Livermore	CeO ₂ Al ₂ O ₃ ?	http://www.cvnanotec.com/
22	Diamond-Fusion International, Inc	San Clemente	Coating	http://www.diamonfusion.com/
23	Docker	San Francisco	Textile	http://us.dockers.com
24	Easton Sports	Van Nuys	Composite mater.	http://eastonsports.com
25	Gap	Pleasanton	Textile	http://gapinc.com
26	Green nanolife	La Palma	TiO ₂	http://www.nanolifeusa.com/index.html
27	Hyper-Therm HTC	Huntington Beach	Composite mater.	http://htcomposites.com/
28	Innovalight	Sunnyvale	Si-ink	http://www.nannovalight.com
29	Intematix Inc.	Fremont	Fuel cell catalyst	http://www.intematix.com/
30	Ishihara corp. USA	San Francisco	TiO ₂	http://www20.inetba.com/ishiharacorpusa/
31	Materia, Inc	Pasadena	Catalyst	http://www.materia-inc.com/index.html
32	Material Methods LLC	Irvine	Composite	http://materialmethods.com/
33	Molecular Nanosystem, Inc	Plao Alto	CNT	http://www.monano.com/
34	MTI corporation	Richmond	TiO ₂	http://www.mtixtl.com/
35	Nanochem (Alex Cripchuck, Inc)	Corona	personal care	http://www.nanochem.org/index.html
36	nanoComposix, Inc	San Diego	Ag, Au, Si powder	http://www.nanocomposix.com/
37	Nanoconduction Inc.	Sunnyvale	CNT	http://www.nanoconduction.com/
38	NanoGram Corporation	Milpitas	Ink, battery mat.	http://www.nanogram.com/
39	NanoH2O	El Segundo	Membrane	http://www.nanoh2o.com
40	Nanomys, Inc	Los Angeles	Si	http://www.nanomyswiss.com
41	Nano scale surface systems(n3s)	Alameda	SiO ₂ coating	http://www.ns3inc.com/
42	Nanostellar, Inc	Redwood City	Pt air catalyst	http://www.nanostellar.com/
44	Nanostructures, Inc	Santa Clara	Si	http://www.nanostructures.com
45	Nanosys, Inc	Palo Alto	Si, GaAs, CdSe	http://www.nanosysinc.com/
46	Nano-Tex LLC	Oakland	Textile	http://www.nano-tex.com/
47	ONMATERIALS LLC	San Diego	Zero valent Fe	http://www.onmaterials.com/
48	Optical components, Inc	Covina	Optical coating	http://www.ocioptics.com/
49	Oxonica	Mountain View	TiO ₂ , CeO ₂	http://www.oxonica.com
50	Pilkington	Lathrop	TiO ₂	http://www.pilkington.com/

51	PowerMetal Technologies, Inc	Carlsbad	Metal alloy	http://www.powermetalinc.com/
52	QuantumSphere, Inc	Santa Ana	Fe, Ag, Cu, Ni, Co	http://www.qsinano.com/
53	Lockheed Martin	Sunnyvale	CNT	http://www.lockheedmartin.com
54	Saint-Gobain	Anaheim	CeO ₂ , SiO ₂ , Al ₂ O ₃	www.innovativeorganics.com
55	Seashell technology	La Jolla	Au, Ag	http://www.seashelltech.com/
56	Simax Technologies, Inc	Irvine	SiO ₂ tubes	http://www.simaxtech.com/
57	Solulink	San Diego	Biomaterials	http://www.solulink.com/
58	sp3 Advanced Diamond Products	Santa Clara	Diamond coating	http://www.sp3inc.com/
59	Spectrum Laboratories	Rancho Dominguez	Bio-membrane	http://www.spectrapor.com/new/
60	Stanford materials	Aliso Viejo	CNTs	http://www.stanfordmaterials.com
61	StClaire	Petaluma	Lubricant	http://www.nanolube.com/index.html
62	Sub-one technology	Pleasanton	Diamond coating	http://www.sub-one.com/
63	Sun Nano	Fremont	CNTs, TiO ₂	http://www.nanomaterialstore.com/
64	Ted Pella	Redding	Au for SEM	www.tedpella.com
65	Transfer Devices, Inc	Santa Clara	Litho. mat., Mask	http://www.transferdevices.com/
66	The North Face	San Leandro	Textile	www.thenorthface.com
67	Unidym, Inc	Menlo Park	CNT conduct. film	http://www.unidym.com/
68	Xterra wetsuits	San Diego	Textile	http://xterrawetsuits.com
69	Aneeeve nanotech	Los Angeles	CNT sensor	www.aneeeve.com

2. Tools and instruments industry

#	Name	Location	Major Products	Web site
1	3D Systems	Valencia	3D-Image	http://www.3dsystems.com/
2	Accurion LLC	Menlo Park	Surface analysis	http://www.nanofilm.de/
3	Agilent Technology	Santa Clara	Nanomech. tester	http://www.chem.agilent.com/
4	Ambios Technology, Inc	Santa Cruz	AFM	http://www.ambiosotech.com/
5	Applied Nanostructures	Santa Clara	AFM probe tip	http://www.appnano.com/
6	Asylum Research	Santa Barbara	AFM	http://www.asylumresearch.com/
7	CRAIC technologies	San Diego	Raman spectroscopy	http://www.microspectra.com/
8	Evans Analytical Group	Sunnyvale	Analysis service	http://www.eaglabs.com/
9	Filmetrics, Inc	San Diego	T.F. measure	http://www.filmetrics.com/
10	Gatan, Inc	Pleasanton	SEM, TEM	http://www.gatan.com/
11	General Nanotechnology	Berkeley	AFM, TEM probe tips	http://www.gennano.com/
12	HENCI system Company	Cardiff	Particle process	http://www.henci.com/
13	Hyphenated-Systems LLC	Burlingame	3D image	http://www.hyphenated-systems.com
14	Intelligent Optical System, Inc	Torrance	Optic instrument	http://www.intopsys.com/
15	JMAR technologies, Inc	San Diego	X-ray	http://www.jmar.com
16	KLA-Tencor Corporation	San Jose	AFM	http://www.kla-tencor.com/
17	Light house worldwide solution	San Jose	Particle counter	http://golighthouse.com/
18	Maxtek, Inc	Cypress	T.F. thickness	http://www.maxtekinc.com/
19	Melles Griot	Carlsbad	Laser, optics	http://www.mellesgriot.com/
20	Multiprobe	Santa Barbara	AFM	http://www.multiprobe.com/
21	NanoAndMore USA	Soquel	AFM probe	http://nanoandmore.com/USA/index.php
22	Nanogea	Westlake Village	AFM	http://www.nanogea.com/
23	NanoMatrix, Inc	Scotts Valley	Nano Fab. service	http://www.nanomatrix.com/
24	Nanometrics, Inc	Milpitas	T.F. thickness	http://www.nanometrics.com/
25	Nanovea Series	Irvine	hardness test	http://www.nanovea.com/
26	Neophotonid Corp.	San Jose	Optic instrument	http://www.neophotonics.com/
27	Opti-Cal	Templeton	Laser optic	http://www.opti-cal.com/
28	Pacific Nanotechnology, Inc	Santa Clara	AFM	http://www.pacificnano.com/
29	Park Systems, Inc	Santa Clara	AFM	http://www.parkafm.com/
30	Particle Sizing system, Inc	Santa Barbara	Measure part. size	http://www.pssnicomp.com/
31	Photometrics Inc.	Huntington Beach	AFM, SEM,...	http://photometrics.net/
32	Quesant Instrument Corporation	Santa Cruz	SPM*	http://www.quesant.com/
33	Righthouse	Fremont	Particle counter	http://www.golighthouse.com/
34	Silicon Genesis Corp.	San Jose	T.F. Machn, Proces.	http://www.siggen.net/
35	Veeco Probes, Inc	Santa Barbara	AFM, deposition	http://www.veeco.com/
36	Wyatt Technology corporation	Santa Barbara	Laser	http://www.wyatt.com/
37	XEI Scientific	Redwood City	Elect. Microscopy	http://www.evactron.com/
38	Xradia, Inc	Concord	X-ray, 3D-image	http://xradia.com/index.html
39	X-tek group	Santa Clara	X-ray	http://www.xtekray.com/

3. Electronic industry

	Name	Location	Products	Web site
1	Advanced Micro Devices (AMD)	Sunnyvale	Semiconductor	http://www.amd.com
2	Applied Materials	Santa Clara	Semiconductor equip.	http://www.appliedmaterials.com
3	Apple	Cupertino	Computing, chips	www.apple.com
4	Aviza Technology, Inc	Scotts Valley	Semiconductor equip.	http://www.avizatechnology.com/
5	Cadence design system	San Jose	IC design, nm range	http://www.cadence.com/us/pages/default.aspx
6	Calient Networks, Inc	San Jose	Fiber optic equip.	http://www.calient.net/
7	CDream corporation	San Jose	Display	http://www.cdreamdisplay.com/
8	Fuji Film Dimatix, Inc	Santa Clara	Printer head	http://www.dimatix.com/
9	Discera, Inc	San Jose	MEMS*	http://www.discera.com/
10	Easic copr.	Santa Clara	Custom Chip	http://www.easic.com/
11	Fujitsu microelectronics america.	Sunnyvale	Electronics	http://www.fujitsu.com/
12	Genesis Microchip inc.	Santa Clara	Image processing chip	http://www.gnss.com/home.phtml
13	Hitachi global storage tech.	San Jose	Hard disks	http://www.hitachigst.com
14	Intel	Santa Clara	Semiconductor	http://www.intel.com/
15	Infineon Tech. North America	San Jose	Semiconductor	http://www.infineon.com
16	Iomega Corp.	San Diego	Storage	http://www.iomega.com/na/landing.jsp
17	Keibaili corporation	Irvine	MEMS*	http://www.kebaili.com/
18	Kovio, Inc	Sunnyvale	SI-based ink for chip	http://www.kovio.com/
19	Luxtera, Inc	Carlsbad	Semiconductor	http://www.luxtera.com/
20	Magma design automation	San Jose	IC design, nm range	http://www.magma-da.com/
21	Microfabrica, Inc	Van Nuys	MEMS*	http://www.microfabrica.com/
22	Nanochip, Inc	Fremont	MEMS*	http://nanochipinc.com/
23	Nanologic, Inc	Walnut Creek	Computing	http://www.nanologic.com/
24	NanoNexus	San Jose	MEMS*	http://www.nanonexus.com/
25	Nisvara, Inc	San Jose	Computing	http://www.silentcomputing.com/
26	Novellus systems, Inc	San Jose	Semiconductor equip.	http://www.novellus.com/
27	ORFID corp.	Pasadena	OLED chip	http://orfid.com/index.html
28	PVA Tepla America, Inc	Corona	Semiconductor equip.	http://www.pvateplaamerica.com/
29	RASIRC	San Diego	Cleaning for Electronics	http://www.rasirc.com/
30	Silicon Genesis corporation	San Jose	Si-processes	http://www.sigen.net/
31	Spansion LLC	Sunnyvale	Semiconductor	http://www.spansion.com/
32	Synopsys, Inc	Mountain View	Chip design	http://www.synopsys.com/
33	Tegal corporation	Petaluma	Semiconductor equip.	http://www.tegal.com/
34	T-Ram Inc.	Milpitas	Semiconductor	http://t-ram.com/index.html
35	Tystar corporation	Torrance	Semiconductor equip.	http://www.tystar.com/
36	Ultratech	San Jose	Semiconductor	http://www.ultratech.com/
37	Vesta Technology, Inc	San Jose	Semiconductor equip.	http://www.vestatechnology.com/

4. Bio-Health industry

	Name	Location	Products	Web site
1	Affymetrix, Inc	Santa Clara	Micro arrays	http://www.affymetrix.com
2	Abraxis Bioscience, Inc	Los Angeles	Tumor medicine	http://www.abraxisbio.com/
3	Apieron	Menlo Park	NO monitor	http://aperon.com/index.html
4	Alnis Biosciences, Inc	Emeryville	Cancer imaging, treatment	http://www.alnis.com/
5	Bioident Technologies, Inc	Menlo Park	Lab-on-chip for life science	http://www.bioident.com
6	Calando Pharmaceuticals Inc	Pasadena	Drug delivery system	http://www.calandopharma.com/
7	Celera genomics	Alameda	Diagnostic platform	www.celera.com
8	Cytoplex biosciences	San Leandro	Biosensors	http://www.cytoplex.com/
9	Eksigent Technologies LLC	Dublin	Protein analysis system	http://www.eksigent.com/
10	Envirosystems Incorporated	Santa Clara	Disinfectant	http://www.envirosi.com/
11	Excellin Life Science, Inc	Milpitas	Cell processing platform	http://www.excellin.com/
12	Fluidigm Corporation	San Francisco	IFC*s for Bio-analysis	http://www.fluidigm.com/
13	GeneFluidics, Inc	Monterey Park	Molecular analysis platform	http://www.genefluidics.com
14	Genencor International, Inc	Palo alto	Enzymes, Bio-products	http://www.genencor.com/
15	Genentech	South S.F.	Life science	http://www.gene.com/
16	Hitachi chem. research center	Irvine	?	http://www.hitachi-chem.co.jp/
17	Insert Therapeutics, Inc	Pasadena	Drug delivery system	http://www.insertt.com/
18	Invitrogen Corporation	Carlsbad	Cell culture, Reagents	https://www.invitrogen.com
19	Labcyte	Sunnyvale	Liquid transfer system	http://www.labcyte.com/default.aspx
20	Lumiphore, Inc	Redwood City	Fluorescent reagents	http://www.lumiphore.com/
21	matrix sensor	Pleasanton	Bio sensor	www.matrixsensorsinc.com
22	Microchip Biotechnologies.	Dublin	?	http://www.microchipbiotech.com
23	Moleculardiamond technologies	Richmond	Diamond	http://moleculardiamond.chevron.com
24	MP Biomedicals LLC	Irvine	Life science, etc.	http://www.mpbio.com
25	Nano Sensors, Inc	Santa Clara	Biosensors	http://www.nanosensorsinc.net/
26	Nanogen, Inc	San Diego	Diagnostic platform	http://www.nanogen.com/
27	Nanomix, Inc	Emeryville	Bio-detection platform	http://www.nano.com
28	Nanostream, Inc	Pasadena	Enzyme detection system	http://www.nanostream.com/
29	Nanosyn, Inc	Menlo Park	Medical chemistry service	http://www.nanosyn.com/
30	Nanotrope, Inc	San Diego	Digitized drug delivery	http://www.nanotrope.com/
31	Parallel synthesis technology	Santa Clara	Si micro array	http://www.parallel-synthesis.com/
32	ProteinX Lab	San Diego	Protein analysis, synthesis	http://www.proteinx.com/
33	SAIC	San Diego	Anticancer vaccines	http://www.saic.com
34	Stemedica	San Diego	?	http://www.stemedica.com/
35	Telomolecular Corp.	Rancho Cordova	Synthetic DNA	http://www.telomolecular.com
36	Trellis Bioscience	San Francisco	Antibody	http://www.trellisbio.com/
37	XDX	Brisbane	Blood test	http://www.xdx.com/

5. Energy industry

	Name	Location	Products	Web site
1	Bloo Solar	West Sac.	Solar cell	http://www.bloosolar.com/index.html
2	Enable IPC	Valencia	Micro battery	http://www.enableipc.com/
3	Front Edge Technology	Baldwin Park	Battery	http://www.frontedgetechnology.com/
4	Kainos Energy Corp.	San Jose	Fuel cell	www.kainosenergy.com
5	Innovalight	Sunnyvale	Solar cell	http://innovalight.com/
6	Nanoexa	Burlingame	Li battery	http://www.nanoexa.com/
7	Nanosolar, Inc	Palo Alto	Solar electricity	http://www.nanosolar.com/
8	PolyFuel, Inc	Mountain View	Fuel cell membrane	http://www.polyfuel.com/
9	Unisun	Newbury Park	Solar electricity	http://members.aol.com/unisun/index.htm
10	Solarmer Energy, Inc.	El Monte	Solar cell	http://www.solarmer.com
11	Ultracellpower	Livermore	Fuel cell	http://www.ultracellpower.com/
12	Miasole	Santa Clara	Solar cell	http://www.miasole.com/index.html
13	Jadoopower Systems	Folsom	Fuel cell	http://jadoopower.com/index.html
14	Pacific fuel cell corp.	Tustin	Fuel cell membrane	http://www.pfce.net/
15	Xsunx	Aliso Viejo	Solar cell	http://xsunx.com/

6. Research institutes

	Name	Location	Homepage
1	California Institute of Technology	Pasadena	www.caltech.edu
2	California Nanosystems Institute	Los Angeles	http://www.cnsi.ucla.edu/
3	Center for Cell Control (NIH nanomedicine center)	Los Angeles	http://www.centerforcellcontrol.org/
4	Center for Functional Engineered Nano Architectonics	Los Angeles	http://www.fena.org/
5	HP Quantum Scicence Research	Palo Alto	http://www.hpl.hp.com/research/qsr/
6	IBM Almaden research center	San Jose	http://www.almaden.ibm.com/
7	Institute for Molecular Manufacturing	Palo Alto	www.imm.org
8	Lawrence Berkeley Laboratory	Berkeley	www.lbl.gov
9	Lawrence Livermore Laboratory	Livermore	www.llnl.gov
10	NASA Ames Center for Nanotechnology	Moffett field	http://www.nasa.gov/centers/ames/home
11	NASA Jet Propulsion laboratory	Pasadena	http://www.jpl.nasa.gov/
12	Palo Alto research center	Palo Alto	www.parc.com
13	San Diego state university	San Diego	http://www.sdsu.edu/
14	San Jose state university	San Jose	http://www.sdsu.edu/
15	Santa Clara university	Santa Clara	http://www.scu.edu/
16	Stanford University	Palo Alto	www.stanford.edu
17	The Burnham Institute	La Jolla	www.burnham.org
18	U. C. Berkeley	Berkeley	www.berkeley.edu
19	U. C. Davis	Daivs	www.ucdavis.edu
20	U. C. Irvine	Irvine	www.uci.edu
21	U. C. Los Angeles	Los Angeles	www.ucla.edu
22	U. C. Merced	Merced	www.ucmerced.edu
23	U. C. Riverside	Riverside	www.ucr.edu
24	U. C. San Diego	San Diego	www.ucsd.edu
25	U. C. San Francisco	San Francisco	www.ucsf.edu
26	U. C. Santa Barbara	Santa Barbara	www.ucsb.edu
27	U. C. Santa Cruz	Santa Cruz	www.ucsc.edu
28	U. of Southern California	Los Angeles	www.usc.edu
29	University of Affiliated Research Center	Los Angeles	http://uarc.ucsc.edu/