

**A Review of the Emerging Nanotechnology Industry:
Materials, Fabrications, and Applications**

**Prepared by
Hai-Yong Kang, Ph.D.**

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**Department of Toxic Substances Control
Pollution Prevention and Green Technology**

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EXECUTIVE SUMMARY

The nanotechnology industry encompasses a wide diversity of potential products and applications. Many nanotech-based products have already been developed and are commercially available. With many additional nanotech-based products presently in their developmental stage and expected to be commercialized in the near future, the industry is poised for rapid growth. Concerns are being expressed about potential risks to workers, public health, and the environment through manufacture, use, and disposition of these newly developed materials with unique and perhaps unknown properties. Because the scope of the nanotechnology industry is broad and involves many different industrial sectors, an understanding of the associated materials, processes, and applications is critical to ensure responsible industry development in a way that both encourages economic growth and protects public health and the environment.

At scales of nanometer range, materials can exhibit unique properties different from their bulk state. Nanotechnology involves manipulating these materials to take advantage of these unique properties. There is great potential for new and improved products in various industrial sectors, including chemicals and materials, health care and biotechnology, electronics and computers, and tools and equipment, as well as defense and security.

To gain an overview of this rapidly growing and diverse industry, literature was reviewed to identify the range of materials and fabrication processes used, as well as the variety of potential products and applications. 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 are discussed in terms of their unique properties, fabrication methods, and applications.

A total of 175 different types of consumer nanoproducts were identified in 9 different industrial sectors. Silver nanoparticles, which are used as an antibacterial agent in 6 different industries, are the most frequently used nanomaterial. Use of carbon nanotubes technology is being widely applied in electronics, automotive, and sporting good products. Also in the automotive industry, nanoclays are increasingly being used to improve structural properties

of plastic polymer composite materials for auto body parts. Titanium dioxide has application in a variety of products, including sunscreens, photocatalysts, photovoltaics, sensors, and self-cleaning catalysts. Nanotechnology is also serving to develop new and improved catalysts, such as with the development of gold and cerium dioxide catalysts.

Further research is needed to determine the effects of these materials and processes on public health and the environment; such as issues are outside the scope of this report.

I. INTRODUCTION

Nanotechnology is a rapidly emerging technology with vast potential to create new materials with unique properties and to produce new and improved products for numerous applications. Many nanotechnology-based products are already available in the marketplace, including sporting goods, electronics, personal care, and automotive parts. However, there is concern that the unique properties of nanomaterials might pose substantial risks, which have been largely unexplored, to both human health and the environment. Understanding the broad scope and diversity of the nanotechnology industry is an important first step in identifying potential risks that may be associated with this industry.

Nanotechnology as a whole is estimated to represent a market of \$11 trillion by 2010, with nanomaterials growing to \$11 billion in 2010 (Pitkethly 2003). Another market research center estimated that the sales of products incorporating nanotechnology will rise from less than 0.1% of global manufacturing output in 2004 to 15% in 2014, totaling \$2.6 trillion (Lux research 2004). Although estimates of future nanotechnology industry growth may differ, they show the great potential of this emerging industry.

Physicist Richard Feynman introduced the concept of nanotechnology in 1959 in his talk “There’s Plenty of Room at the Bottom.” Feynman introduced new ways of thinking of manipulating and controlling materials on a small scale, such as the atomic and molecular levels, in various fields (Caltech). Norio Taniguchi first used the term “nanotechnology” in 1974 to explain precision engineering in semiconductor processes (Taniguchi 1974). In 1985, fullerene, which is shaped like a ball and just 1 nanometer in diameter, was discovered by Richard E. Smalley. In 1991, Sumio Iijima discovered carbon nanotubes, which are tube-shaped materials whose diameter measures on the nanometer scale (IEEE).

The American Society for Testing Materials (ASTM) international standard defines nanotechnology as a wide range of technologies that measure, manipulate, or incorporate materials and/or features with at least one dimension between approximately 1 and 100 nanometers (nm).¹ Such applications exploit the properties, distinct from bulk/macroscopic systems, of nanoscale components (ASTM). Within the nanometer size range, different size particles of the same material may exhibit different mechanical, thermal, optical, and

¹ 1 nm = 10^{-9} m. Thickness of human hair is about 80×10^{-6} m = 80,000 nm. Also, there are other efforts to define the term ‘nanotechnology’ with different size limits.

electrical properties. Quantum dots of the same element, for example, are clusters of atoms less than tens of nanometers in size that emit different colors depending on their specific particle size.

As particle size decreases, the ratio of surface area to volume rapidly increases so that surface properties become the dominant factor. This large surface area provides various unique properties that have widespread applications in many different industrial sectors, including the composite materials, electronics, and chemical sectors.

Many new and exciting nanomaterials and products have been developed. Carbon-based nanomaterials include carbon nanotubes (CNTs), fullerenes, carbon nanofibers, and carbon black. Small additions of nanomaterials such as carbon nanotubes can greatly improve structural properties of composite materials. Due to their electrical conductivity, carbon nanotubes also have application for the manufacture of low-cost solar cells, electronics, and anti-static composite materials. Titanium dioxide (TiO_2) nanoparticles have a large band gap and are used for ultraviolet (UV) protection, photocatalysts, photovoltaics, and sensing. As a photocatalyst, TiO_2 nanomaterials are being applied to exterior walls of buildings to provide a self-cleaning function. Nanoclay in combination with nylon is used to increase structural hardness in plastic polymer nanocomposite materials. ThermoPlastic Olefin (TPO) and polypropylene (PP) based nanocomposite materials are used for automotive parts. In quantum dots, simply altering the size of materials, the band gap energy changes, and the light emitted changes color. These semiconductor quantum dots are used in biolabeling and anti-counterfeiting applications to create special inks, dyes and paints, light displays, and chemical sensing. Silver (Ag) nanoparticles have been found to be very effective as an anti-bacterial agent and are used in many types of products. Gold (Au) nanoparticles less than 5 nm in diameter can be a very effective catalyst for several chemical reactions under ambient temperature. Cerium oxide (CeO_2) can be used as a diesel fuel combustion catalyst, which reduces fuel consumption, carbon monoxide (CO) emissions, and other harmful exhaust emissions.

However, in contrast to the benefits of nanotechnology, concern has been raised about potential adverse effects to humans and the environment. Several possible adverse effects of nanomaterials, such as oxidative stress by TiO_2 , penetration of zinc oxide (ZnO) particles into animal skin, and structural resemblance of carbon nanotubes to asbestos, have been

reported (Brayner 2008). Additionally, the end-of-life impacts of nanomaterials to human and the environment are largely unknown. Further research will be needed to better understand and possibly mitigate the risks posed by nanomaterials. Understanding the broad scope of this industry is a first step in preventing possible adverse impacts to human health and the environment, and encourages responsible growth of this industry. Moreover, understanding issues related to current technologies will serve to promote less harmful and/or safer alternative technologies for the future.

This report reviews the different types of nanotechnologies, nanomaterials and related products that have been developed, and their use. Currently available nano-consumer products are identified for each industrial sector. Included is an extensive review of nanoparticle characterizations (size, shape, and type), properties (mechanical, thermal, optical, and electrical), and synthesis or fabrication methods. The report analyzes current and future applications of nanomaterials and technologies.

II. CARBON-BASED NANOMATERIALS

Carbon-based nanomaterials are produced and used in many industrial sectors. These materials include carbon nanotubes, fullerenes, carbon nanofibers, carbon black, and carbon onions. Arc discharge, chemical vapor deposition (CVD), and laser ablation are major methods for fabrication of these materials (except carbon black), and by changing fabrication conditions, the properties of carbon-based nanomaterials can be changed. In CVD, just changing chamber conditions can change the types of carbon materials deposited on the substrate. For example, changing of reaction temperature, input gas concentration, or pressure alters the types and properties of carbon nanotubes (Obraztsov 2004).

2.1 Carbon nanotubes (CNTs)

A carbon nanotube is a tubular form of carbon with a diameter as small as 1 nm and length of a few nanometers to a micron. CNT is configurationally equivalent to a two-dimensional graphene sheet rolled into a tube. Carbon nanotubes have potential for use in many industrial sectors. For example, carbon nanotubes are used in the automotive, electronic, energy, and bio-health industries. Several methods are used to synthesize carbon nanotubes such as arc discharge, CVD and laser ablation, and commercial suppliers are currently available worldwide from small laboratory scale to mass production scale. However, to use carbon nanotubes, pretreatment such as purification and/or surface modification of the carbon nanotubes is necessary.

There are two types of carbon nanotubes: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). Figure 2.1 shows images of single- and multi-walled carbon nanotubes. Single-walled CNTs contain only one wall, but multi-walled CNTs can contain two or more walls. Based on the rolling direction, CNTs can be semiconductors or conductors. Carbon nanotubes show extraordinary mechanical, electrical, and thermal properties because of their C-C covalent bonding and seamless hexagonal network architecture (Meyyappan 2004).

The automotive industry uses CNT composite materials because of their light weight and conductivity. High electrical and thermal conductivities of CNTs are utilized by the electronic industry, with potential application as field emitters or conductive transparent films. Batteries and solar cells use CNTs for their high electrical conductivity. Because of

their light weight and structural strength, CNT composite materials are used in sporting goods such as tennis rackets and baseball bats. In the bio-health industry, CNTs can be used as sensors. Companies involved with CNTs are listed in Appendix II.

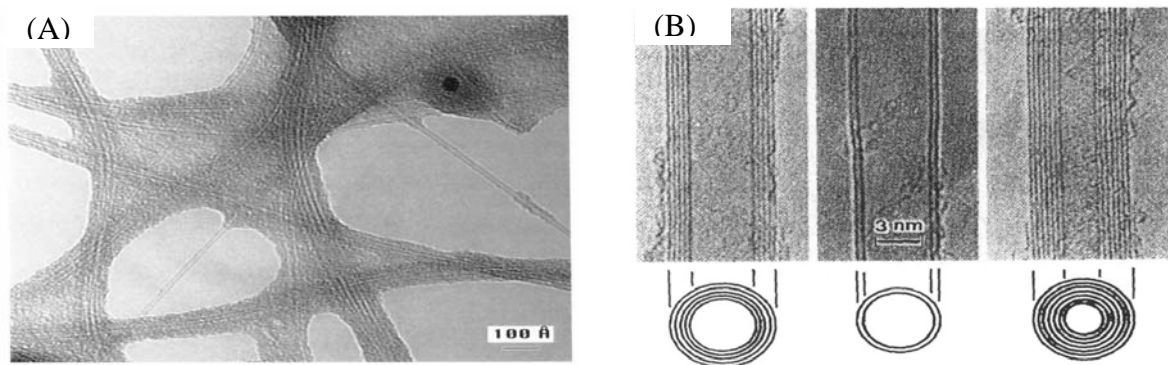


Figure 2.1 Single- and multi-walled carbon nanotubes. (A): Single-walled carbon nanotube (Bethune 1993). (B): Multi-walled carbon nanotube (Iijima 1991).

2.2 Fullerene

Fullerenes are cage-structured carbon molecules in a spherical shape with a wide range of sizes and molecular weights such as C_{60} , C_{70} , C_{76} , and C_{84} . The C_{60} fullerene (buckminsterfullerene or Buckyball) is the representative and approximately 0.7 nm in diameter. In the fullerene structure, all C sites are equivalent and the bond lengths are 0.14 nm for the double bond and 0.146 nm for the single bond. Figure 2.2 is a representation of a C_{60} fullerene molecule. Physical and chemical properties may be tuned via the addition of element and molecular species into the fullerene lattice ($C_{59}N$), within the cage (N at center of C_{60}), or coating the surface of fullerene with transition metals (Moriarty 2001). These properties can be used for drug delivery, facial creams, moisturizers, lubrications, trace monitors, and electronic circuits.

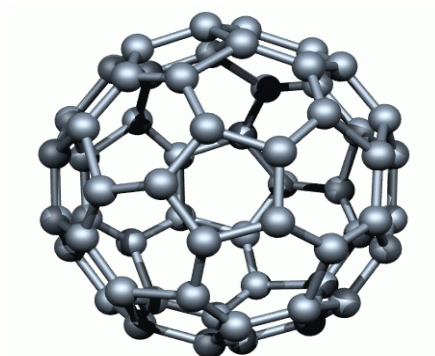


Figure 2.2 Representation of a fullerene molecule (GTRI).

Fullerenes are produced using electric arc discharge or thermal CVD processes. In the arc discharge process, fullerenes cannot be produced if hydrogen atoms are present in the reaction gas (Ando 2004). Companies that produce fullerenes are listed in Appendix II.

2.3 Carbon onion

Carbon onion is one of the fullerene-related materials having concentric graphitic shells. Its particle size is about 10 nm in diameter. Ideally the center shell is a C_{60} molecule. These particles can be made by high-energy electron bombardment on carbon soot, heat treatment of soot or diamond clusters, carbon implantation into copper or silver substrate, plasma chemical vapor deposition, and arc discharge methods (Chen 2001; Cabioch 1995).

To make carbon onion with carbon implantation, 120 KeV carbon ions implant into crystalline copper substrate at 700° to 1000°C. During the process, 10^{-5} Pa of vacuum is maintained. Carbon onions are formed on the surface of substrate. Schematic diagram of chamber and image of carbon onion are shown in Figure 2.3 (Cabioch 1995). These carbon onions are 5 to 10 nm in size and can be used for solid lubrication.

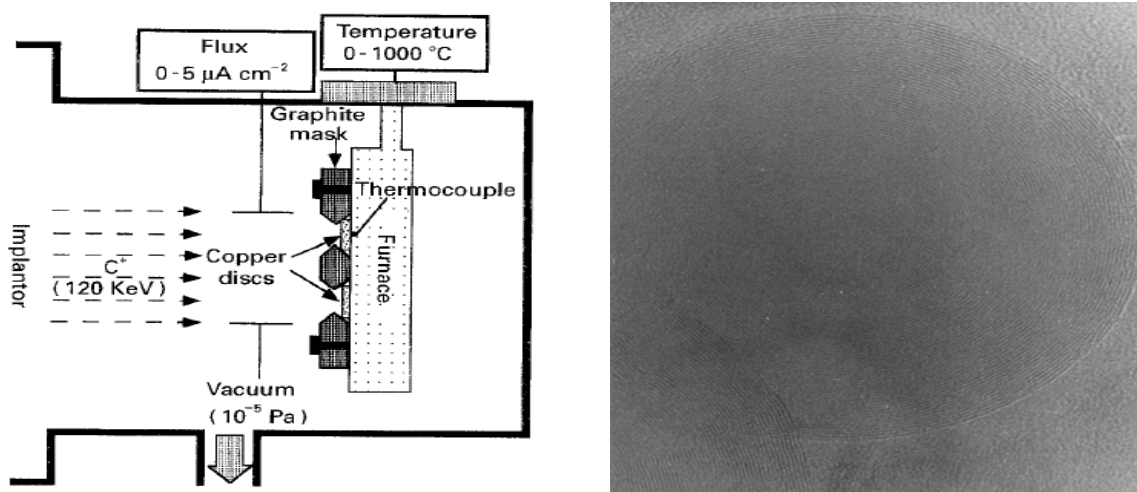


Figure 2.3 Schematic diagram for implantation of carbon and image of carbon onion (Cabioch 1995).

2.4 Carbon black

Carbon black is pure elemental carbon in the form of colloidal particles. It is produced by incomplete combustion or thermal decomposition of gaseous or liquid hydrocarbon under

controlled conditions. The furnace black and thermal black processes are used to make carbon black, but the furnace black process is the most common commercial process. The average particle size of carbon black is a few nm. The primary use of carbon black is in rubber products (approximately 90%), mainly tires and other automotive rubber products such as hoses, gaskets, and coated tubes. About 9% of carbon black is used for pigment in toners and inks, and the remaining 1% is used as an ingredient in hundreds of diverse applications. Much smaller amounts of carbon black are used in the manufacture of dry-cell batteries (ICBA; VDI).

2.5 Carbon nanofiber

Arc discharge deposition with hydrogen gas is used to produce carbon nanofibers. Carbon nanofibers have a very narrow inner cavity or practically no hollow channel in their center, and the graphitic layers at the tips are defective or partially broken. For example, carbon fibers have an innermost diameter that is smaller than independently produced MWCNTs (Meyyappan 2004; Robertson 2004), the radius of the curvature at the tip is less than 3 nm, and the diameter of the innermost layer is less than 1 nm (Saito 2000).

Carbon nanofibers also can be fabricated by thermal CVD using templates (Wu 2004). Anodic aluminum oxide (Al_2O_3) with a thickness of 30 μm and pores of about 200 nm in diameter is used as the template. After deposition of carbon materials through the pores, carbon nanofibers remain after removal of the template. Carbon nanofiber can be used for filler in composite materials or electron emitters like CNTs.

A transmission electron microscopy (TEM) image of nanofiber produced by hydrogen gas arc discharge is shown in Figure 2.4 (Saito 2000). It shows an extremely narrow channel in the center. The diameter of the innermost layer is only about 1 nm.

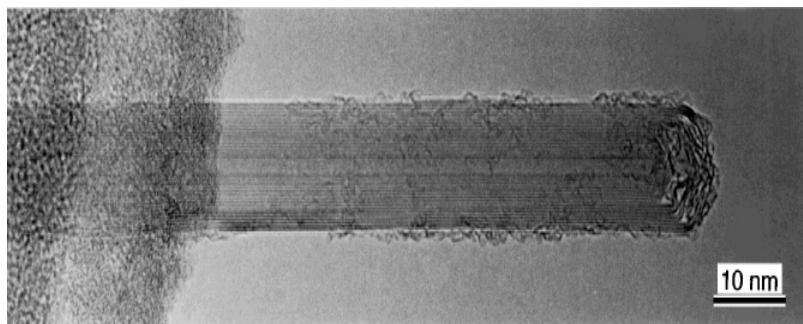


Figure 2.4 Carbon nanofiber produced in a hydrogen gas arc discharge.

III. NANOCOMPOSITE MATERIALS

3.1 Polymer matrix composite materials

Nano-size filler materials provide new opportunities for improving plastic composite materials. Different from conventional standard fillers, nanocomposite materials require only a very small amount of nano-filler (less than 5 wt%) to yield marked improvements in mechanical, thermal, electrical, and other properties such as gas impermeability, dimensional stability, and flame retardance. Furthermore, all of these benefits are available without sacrifices in composite density or light transmission of matrix resins.

Nano-fillers provide one to three orders of magnitude more interfacial area per particle than conventional mineral filler (Vaia 2004). Two types of nano-filler that are used in commercial products are nanoclays and nanotubes, such as carbon nanotubes and aluminum silicate nanotubes (NaturalNano). Both types of nano-filler materials require surface modification prior to use.

3.1.1 Applications of polymer matrix nanocomposite materials

Nanoclay and carbon nanotubes are the key nano-elements used in polymer nanocomposite materials. Current major applications of plastic nanoclay composite materials include automotive parts, such as automotive body panels and under-hood components, and packaging. In packaging, nanocomposites decrease the permeation rate of gases and moisture vapor into plastic by creating a “tortuous path.” Nanocomposites can also provide materials of high stiffness and impact resistance that are used for electrical parts, power-tool housing, appliance components, pallets, and dunnage.

Toyota produced the first commercial nanocomposite materials on the market, a timing belt cover and food packaging, based on nylon 6 with nanoclays. After that, many other companies produced plastic nanocomposite materials for packaging and automotive parts. Nanoclay can also be applied to reinforce fabrics. By adding 1 wt% of nanoclay, mechanical properties of polypropylene fabrics are improved (Bhat 2008). Nanoclay can potentially also be used in thermoplastic/natural fiber composites to improve their mechanical properties (Lei 2007).

It is estimated that the total worldwide market for polymer nanocomposites was 24.5 million lbs and \$90.8 million in 2003, and that the market will grow at an average annual rate of 18.4% to reach \$211.1 million by 2008 (PT 1999; PT 2004).

3.1.2 Clay-polymer composite materials

3.1.2.1 Structure of clay material

Nanoclays for plastic composite refer to a category of clay minerals with a specialized structure, characterized by plate morphology. The most widely used nanoclay for plastic composite is modified montmorillonite clay. Montmorillonite is a 2-to-1 layered smectite clay mineral with a platy structure. Each layer has 2 tetrahedral sheets containing an octahedral sheet between them. Individual platelet thicknesses are just one nanometer, but surface dimensions are generally 300 to more than 600 nanometers, resulting in an unusually high aspect ratio. Hundreds or thousands of these layers are stacked together with van der Waals forces to form clay particles.



Figure 3.1 A platelet montmorillonite structure (OMNI Lab).

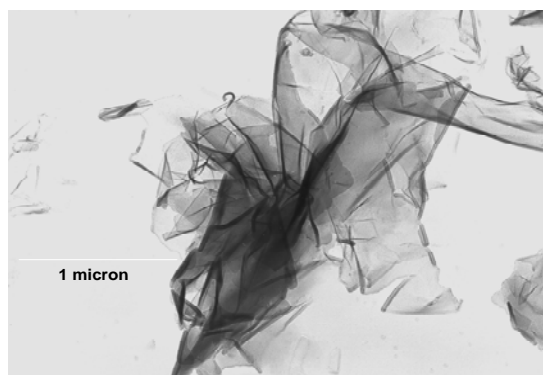


Figure 3.2 TEM of refined montmorillonite (Southern clay products).

Figure 3.1 shows platelets shape of nanoclays and Figure 3.2 shows transmission electronic microscopic image of refined nanoclays. The thickness of these nanoclay platelets is only 1 nm, less than the wavelength of light, so they do not impede light's passage.

3.1.2.2 Characteristics of clay material

For commercial applications, nanoclays must first be modified in a two-step process. Once modified, the treated clay can then be incorporated into the resin matrix either during polymerization or by melt compounding. In the first step, the hydrophilic surface property of

natural existing montmorillonite must be changed to hydrophobic for compatibility with organophilic polymers that are generally used in composites. The most popular surface treatment method exchanges organic ammonium cations with existing inorganic cations on the clay's surface. These modified clays are known as organoclays.

Nanoclays normally exist as agglomerated bundles, consisting of thousands of platelets held together by van der Waals force. In the second step, the clay is exfoliated, which is separation of the individual clay platelets from each other. To optimize the gas barrier function and promote good clarity of packaging materials, the platelets must be fully exfoliated in the plastic matrix. However, complete exfoliation is not always good for composite materials. For example, complete exfoliation in polyolefin material decreases particle reinforcement, which may be a problem for automotive application (Jarus 2005; Nanocor).

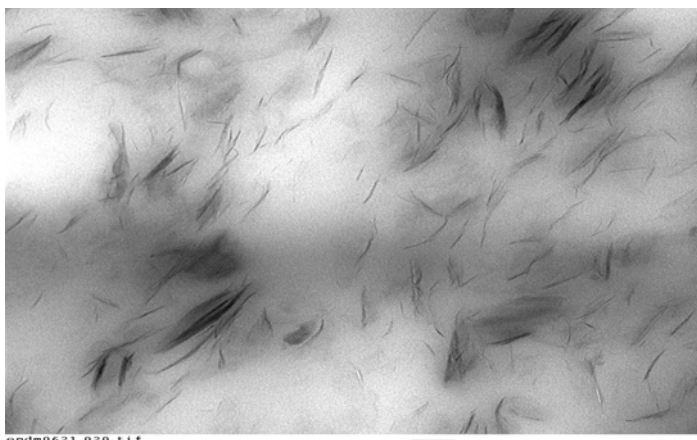


Figure 3.3 Dispersion of exfoliated nanoclays in resin matrix, ethylene propylene diene monomer (Yoon 2006).

By combining surface compatibilizing agents and process shear, commercial nanoclays can achieve more than 95% of exfoliation and even distribution within polyamide plastics (Maul, 2005). Figure 3.3 shows the dispersion of exfoliated nanoclay within a plastic resin matrix.

3.1.2.3 Fabrication methods

3.1.2.3.1 In situ polymerization

Polymer precursors are inserted between the clay layers, causing them to expand. The expanded clay layers are then dispersed into the matrix by polymerization. This method can produce well-exfoliated nanocomposites applicable to a wide range of polymer systems, and is particularly useful for thermosetting polymers (Gao 2004).

3.1.2.3.2 Solution-induced intercalation

This method uses solvent to swell and disperse clays into a polymer solution. It is mainly used for water-soluble polymers² because of the low cost of water as a solvent as well as its low health and safety risk. In addition, this method can be used for commercial production. However, this method is not applicable to most engineering (i.e., non-water soluble) polymers because of high solvent cost, and health and safety concerns (Gao 2004).

3.1.2.3.3 The melt process

During the melt process, clays and polymers are intercalated with each other. The efficiency of intercalation is lower than in situ polymerization and often produces a partially exfoliated structure. However, this method can use traditional techniques such as extrusion and injection molding to produce nanocomposites and is easily adapted to commercial production (Gao 2004).

3.1.2.4 Applications

3.1.2.4.1 Barrier for packaging

A combination of nylon and nanoclay is used for barrier layers in multilayer polyethylene terephthalate (PET) bottles and films for food packaging. Nanoclays in composite materials act as a barrier and create a “tortuous path” for gas molecules to go through the matrix resin. This tortuous path hinders the permeation of gases when they attempt to penetrate a plastic matrix. Also, because nanoclays do not degrade in the matrix, the gas barrier property is maintained over time. These clay nanocomposites are used for oxygen (O₂) and carbon dioxide (CO₂) sensitive products (Lan 2001). Figure 3.4 shows a schematic diagram of tortuous path due to the exfoliated nanoclay in matrix resin.

² There are several types of water soluble polymers such as Partially hydrolyzed polyacrylamide (HPAM), xanthan gum, guar gum, carboxymethylcellulose (CMC), and hydroxyethylcellulose (HEC).

The major resin material for gas-impermeable plastic packaging is nylon 6. The focus is on PET bottles, where nanocomposites provide a gas-impermeable barrier to oxygen and carbon dioxide, and mechanical strength. Nylon 6 with 2 wt% nanoclay has three times the oxygen barrier property than that of neat nylon 6 (PT 2001). Adding 5 wt% nanoclay increases the Young's Modulus and reduces the oxygen transfer rate (OTR³) by five times. The results are shown in Table 3.1 (Maul 2005). Improved clarity is also reported (PT 2001).

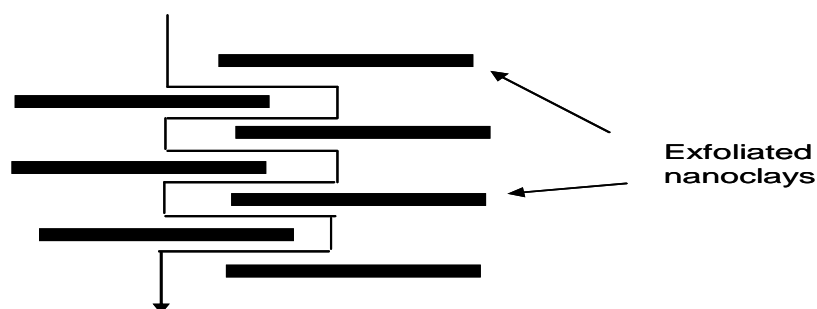


Figure 3.4 Schematic diagram of tortuous path due to exfoliation of nanoclays.

Mitsubishi Gas Chemical's nylon nanocomposite is used commercially in Europe in multi-layer PET bottles for beer and other alcoholic beverages. Honeywell's nanocomposites are used commercially for beer bottles in Korea and provide a 26-week shelf life. Honeywell also considers nanocomposite materials as replacement for ethylene vinyl alcohol copolymer (EVOH, which is a barrier resin for use in food and nonfood packaging applications) in film and pouches. LG Chem. Ltd. of Korea has developed high-barrier monolayer blow-molded container of high-density polyethylene (HDPE) with 3 to 5 wt% nanoclay for holding toluene (PT 2004). InMat Inc. used elastomeric nanocomposite barrier coating for commercialization of Wilson's Double Core tennis ball in 2001 (PT 1997).

Material	Young's Modulus (MPa)	OTR (cc-mil/100in ² -day)
PA (Nylon) 6	140	2.91
PA (Nylon) 6 + 5 wt% nanoclays	705	0.58

Table 3.1 Changes of Young's modulus and OTR in polyamide (PA) 6.

³ The OTR is measured in O₂ mass/time

3.1.2.4.2 Automotive parts

Nanoclay is used to increase structural strength in plastic polymer nanocomposite materials because of its relative low cost (\$2.25~3.25/lb as of Nov. 2004) compared to carbon nanotubes. ThermoPlastic Olefin (TPO) and polypropylene (PP) based nanocomposite materials are used for mainly automotive parts (PT 2004). It is expected that the auto industry will increase usage of nano-PP, mostly to displace existing PP applications. PP nanoclay composite is used in the car seat back on the Acura TL 2004 and center console for a 2006 light truck, and in office furniture (PT 2001).

TPO nanocomposites provide strength equivalent to the talc-filled PP it replaces, and a 7% to 8% weight savings. Furthermore, TPO nanocomposites improve low-temperature impact strength and surface quality. TPO clay nanocomposite materials are used in GM's van (2.5 wt% nanoclay in a step-assist for Astro van, Safari in 2002), the body side molding on 2004 Chevrolet Impala, and the cargo bed on the 2005 GM Hummer sport utility truck (see Figures 3.5 and 3.6) (PT 2001; PT 2004).



Figure 3.5 Impala side moldings with nanoclay composite material (Southern Clay Products).



Figure 3.6 Hummer cargo bed with nanoclay composite material (PT 2004).

3.1.2.4.3 Flame retardant

For flame-retardant nanocomposites, polyolefin, polystyrene (PS), and PP resin are generally used for the matrix. These resins readily form char layers when exposed to heat. This char formation impedes the movement of volatilized polymer from the interior of a plastic matrix to the surface, which decreases the mass loss rate and flammability. The optimal loading amount of nanoclays to reduce flammability is 5 wt% (Gilman 2003). It is reported that for 5

wt% of nanoclays added, the peak heat release rates (HRR⁴) are reduced by 70% (Lan 2001). When nanoclays are used together with traditional flame retardant, nanocomposites can achieve equivalent effect using significantly less flame-retardant additive.

The National Institute of Standards and Technology (NIST) found that 2 to 5 wt% levels of nanoclay in nylon 6 reduced the rate of heat release by 32% to 63%. Also, Foster Corp. demonstrated that a higher level (13.9 wt%) of nanoclay can be added to nylon 12 to improve fire protection, and it introduced nylon 12/nanoclay compounds for tubing and film in 2001 (PT 1999; PT 2004).

3.1.2.5. Suppliers of nanoclay composite materials

Table 3.2 lists a number of representative suppliers of nanoclay composite materials. Domestic suppliers of nanoclay include NanoCor and Southern Clay Productions, Inc.

Supplier & Trade name	Matrix Resin	Nano-Filler	Target Market
Bayer AG (Durethan LPDU)	Nylon 6	Organo-clay	Barrier films
Clariant	PP	Organo-clay	Packaging
Honeywell (Aegis)	Nylon 6 Barrier Nylon	Organo-clay Organo-clay	Multi-purpose Bottles and film
Kabelwerk Eupen of Belgium	EVA*	Organo-clay	Wire & cable
Lanxess (Durethan)	Nylon 6	Clay	Barrier
Nanocor (Imperm)	Nylon 6 PP Nylon MDX6	Organo-clay Organo-clay Organo-clay	Multi-purpose Molding PET beer bottles
NanoPolymer (Nanomide)	Nylon 6	Clay	Barrier
Nycoa (NycoNano)	Nylon 6	Clay	Barrier
Polymeric Supply	Unsaturated polyester	Organo-clay	Marine, transportation
PolyOne (Nanoblend)	Nylon 6	Clay	Barrier
RTP	Nylon 6, PP	Organo-clay	Multi-purpose, electrical
Showa Denko (Systemer)	Nylon 6 Acetal	Clay, mica Clay, mica	Flame retardance Multi-purpose
Ube (Ecobesta)	Nylon 6, 12 Nylon 6, 66	Organo-clay Organo-clay	Multi-purpose Auto fuel systems
Unitika	Nylon 6	Organo-clay	Multi-purpose
Yantai Haili Ind. & Commerce	UHMWPE**	Organo-clay	Earthquake-resistant pipe
Southern Clay Production	Polymer	Organo-clay	Multi-purpose
Foster Corp.	Nylon 12	Clay	Flame retardant

Table 3.2 Representative suppliers of nanoclay composite materials

* Ethylene-vinyl acetate

** Ultra-high molecular weight PE

⁴ The rate that heat is generated by fire. The HRR is measured in Joules per second (Watts).

3.2. Metal matrix composite materials

Metal matrix composites (MMCs) are a relatively new category of engineering materials that can be tailored to meet specific needs for high impact and wear resistance, high melting point, chemical resistance, and high neutron absorption capacity. MMC research and development activity has been concentrated on aluminum alloys because of their low densities. Nanocrystalline aluminum alloys reinforced with particular ceramics such as boron carbide (B_4C), silicon carbide (SiC), and boron nitride (BN) can significantly enhance mechanical properties.

Mechanical milling is a typical method to produce MMCs. Newly developed cryomilling technology is capable of producing a nanocrystalline grain metallic powder. Using this fine nanocrystalline grain powder achieves greater strength in the matrix. Cryomilling, which is mechanical milling at cryogenic temperature, takes advantage of both the extremely low temperature of the liquid nitrogen medium and the attributes associated with conventional milling. This technique is available to produce nanoscale materials in large quantities.

3.2.1 Cryomilling process

A mixture of elemental or pre-alloyed powders is ground using attrition or shaker mills that generate high-energy compressive forces. In attrition mills, powders with typical particle sizes less than about $50\mu m$ are placed together with a number of hardened steel or tungsten carbide (WC) coated balls. The resulting metal matrix composite powders can be shaped with extrusion or other processes. Metal matrix composites can be used for the aerospace or automotive industry because of their hardness and light weight. Figure 3.7 shows the mechanism for producing a composite material and a TEM image for a cryomilled aluminum/boron carbide (Al/B_4C) composite powder (VDI; Ye 2006).

To make an aluminum MMC material, Al powder with particle size of 40 to $44\mu m$ and B_4C powder with 1 to $14\mu m$ particle size are cryomilled. During the milling process, liquid nitrogen is supplied to maintain extremely low temperature. After cryomilling, the matrix grain size of Al is reduced to 24 to 27 nm , and B_4C particle size is reduced to 0.2 to $2\mu m$ (Ye 2006).

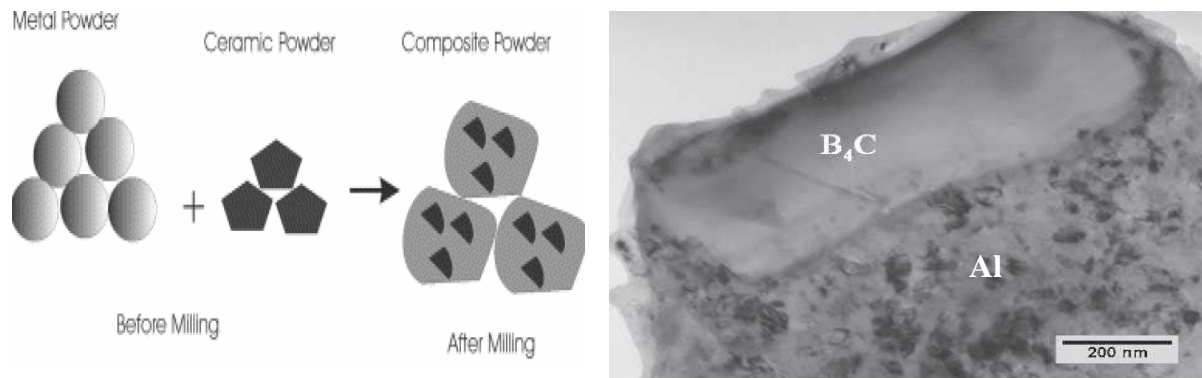


Figure 3.7 Schematic diagrams showing the formation of composite powder and transmission electron microscopic image for the Al/ B_4C composite powder cryomilled.

IV. QUANTUM DOTS

4.1 Definitions and markets for quantum dots

At dimensions in the atomic size range, crystalline materials behave according to the rules of quantum physics. When semiconductor materials absorb sufficient energy, electron-hole pairs are created, which are called excitons. Excitons have an average physical separation between electron and hole, and this physical distance is different for each semiconductor material. If the crystalline dimension of the semiconductor particle falls below the size of the exciton Bohr radius, the electron energy levels become discrete, and the crystalline materials become quantum dots (QDs). Figure 4.1 shows density of state and energy for bulk and quantum dot.

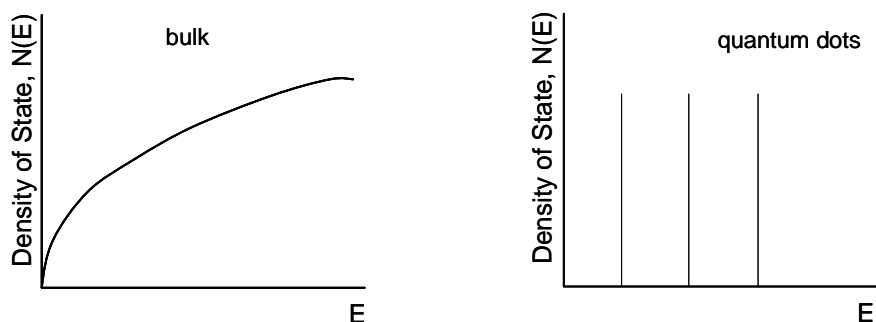


Figure 4.1 Density of state and energy for bulk and quantum dot (modified from Jacak 1998).

The diameter of a quantum dot is on the order of the exciton Bohr radius and less than 10 nm. Within the regime of these critical dimensions, quantum dots exhibit distinctly different behavior from their bulk form in optical, electronics, and magnetic properties. Generally, quantum dots fall into the category of nanocrystals and include quantum rods and quantum wire. Nanocrystalline semiconductors are the most widely used quantum dot materials.

The global market for QDs is projected to reach more than \$700 million by 2013. The current commercial application is in life sciences. The biggest growth sector will be in optics for QD-based lasers and other optical components in telecommunications. The other growth sector is in electronics for QD-based flash memory and optoelectronics in lighting and displays (electronics).

4.2 Properties and structures of quantum dots

The band gap of quantum dots depends on the particle size of the material. This is the most predominant feature of quantum dots. By changing the particle size, the band gap will change, and so will the color of light emitted. This occurs because the specific wavelength of light emitted is a function of the band gap energy.

When material is reduced in size to the atomic level, the energy band is broken into discrete levels so that the band gap is widened. This means that the absorption and emission wavelength both become shorter. The smaller quantum dots have larger band gap energy. Thus, by simply altering the size of materials, we can change the band gap energy, e.g., we can change the color of light emitted because emission color from quantum dot depends on band gap energy. Varying the size and composition of quantum dots determines the color of emitted light. Cadmium sulfide (CdS), zinc selenide (ZnSe), cadmium selenide (CdSe), indium phosphor (InP), and indium arsenic (InAs) are examples of quantum dots. Figure 4.2 shows schematic relationships between band gap and photon energy (Linsebigler 1995; Rogers 2008) and color of quantum dots according to size of dots (Ocean NanoTech).

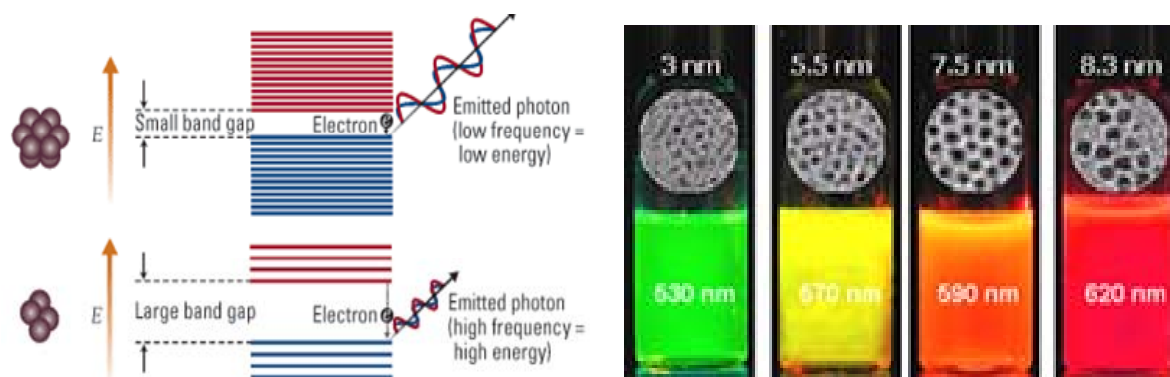


Figure 4.2 Schematic diagrams of band gap and photon energy (Rogers 2008), and changing color of quantum dots according to size of dots (Ocean NanoTech).

Generally, quantum dots have a core/shell structure. The diameter of the semiconductor core is smaller than the material's exciton Bohr radius, which is a material specific property. For example, the exciton Bohr radius of CdSe quantum dot is 5.3 nm (Bukowski 2002)⁵. The shell is composed of several atomic layers of an inorganic wide band gap semiconductor. The core/shell structure results in brighter emission when the shell is of a different semiconductor material with a wider band gap than the core semiconductor material

⁵ The exciton Bohr radius of Ge is 17.7 nm and that of Si is 4.9 nm (Cullis 1997).

(Evident; Rogers 2008). By themselves, the emissions of semiconductor cores are relatively weak and quite unstable. By encapsulating these cores with a high band gap material that is structurally related, the emission intensity and stability are enhanced. For example, the CdSe/CdS core/shell structure quantum dots enhance the property of plain CdSe quantum dots (Li 2003).

However, these core/shell quantum dots are not soluble in water, which limits their biological usages. To overcome this, an outer coating, such as a polymer layer⁶, is added to make the quantum dot water-soluble and allow for conjugation to the biomaterial (Invitrogen). Figure 4.3 shows the schematic diagram of a polymer-coated core/shell quantum dot for conjugation to biomaterials.

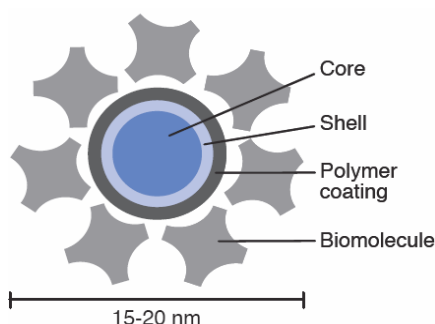


Figure 4.3 The schematic diagram of polymer coated core/shell quantum dot (Invitrogen).

4.3 Fabrication methods for quantum dots

There are several methods for fabrication of quantum dots: molecular beam epitaxy (MBE), electron beam lithography and MBE, metal organic chemical vapor deposition (MOCVD) and colloidal synthesis. Each method has some advantages and different applications. Figure 4.4 shows an image of a quantum dot array, indium-gallium-arsenic/aluminum-gallium-arsenic (InGaAs/AlGaAs), by MOCVD.

4.3.1 Colloidal process

This method is a potentially low-cost mass-production process that creates quantum dots in a liquid. Colloidal semiconductor quantum dots have great interest due to size-specific properties and flexible processing chemistry. The size of quantum dots can be controlled in this process by the time duration that quantum dots remain in the solution.

⁶ Amine, carboxyl, biotin, and streptavidin

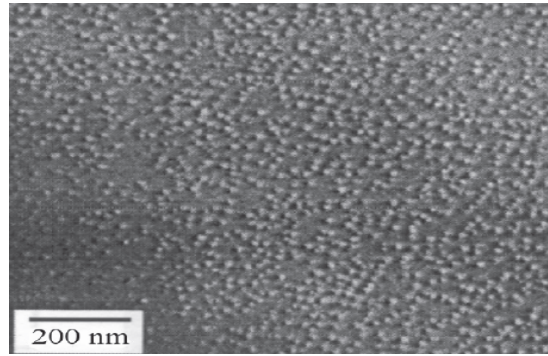


Figure 4.4 Quantum dot arrays of InGaAs/AlGaAs (Grundmann 2000).

In a 2003 report, J.J. Li et. al. described the raw materials and synthesizing processes required for fabrication of CdSe/CdS structure (Li 2003). Materials used to synthesize the CdSe/CdS core/shell quantum dots included cadmium oxide, selenium powder, tributylphosphine (TBP), sulfur powder, tricetylphosphine oxide (TOPO), 1-octadecene (ODE), oleic acid (OA), octyldecylamine (ODA), and stearic acid.

For synthesis of CdSe core nanocrystals, mixtures of CdO, stearic acid, and ODE are first heated up to 200°C to produce a colorless solution. After cool-down to room temperature, ODA and TOPO are added and then heated up to 280°C with argon (Ar) flow. A solution of dissolved selenium (Se) in TBP and ODE is then added and CdSe nanocrystals (3.5 nm) are precipitated. The second step is fabrication of CdS shell on the core surface. Solutions of cadmium oxide (CdO) dissolved in oleic acid and sulfur dissolved in ODE are sequentially added to finish the core/shell structure (Li 2003). Washing with methanol and hexane, and centrifuging and are two methods used to purify and extract quantum dots. (Li 2003; Asokan 2005). Figure 4.5 shows the process flow for synthesis of CdSe/CdS structure.

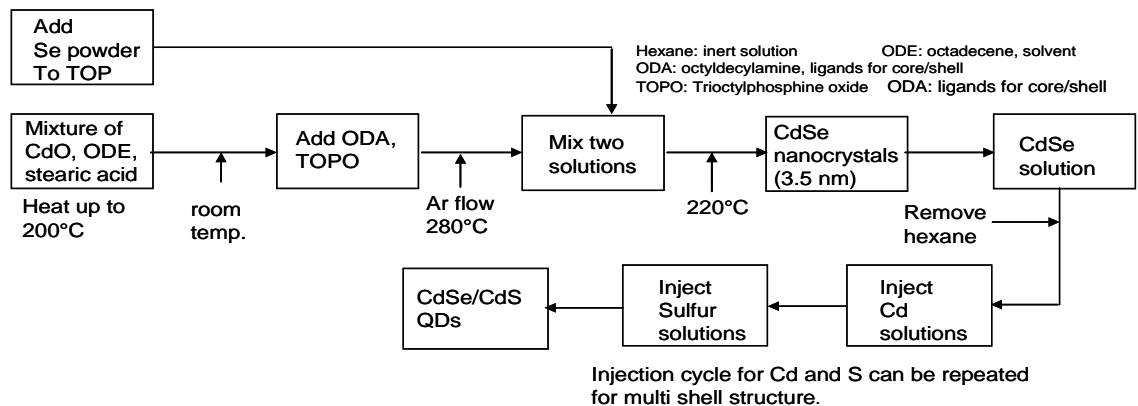


Figure 4.5 Process flow for synthesis of CdSe/CdS structure.

4.3.2 Molecular beam epitaxy (MBE)

MBE is a method that deposits layer by layer of crystals on a substrate. Pure elements are evaporated, then condensed and combined on the surface of the substrate under a vacuum condition. The term "beam" refers to evaporated atoms that do not interact with each other or vacuum chamber gases until they reach the substrate. Quantum dots fabricated by this method are used for quantum computation, but the cost is high and positioning of dots can't be controlled. For indium arsenic/gallium arsenic (InAs/GaAs) systems, In and As atoms are deposited on GaAs substrate to form an epitaxial layer. A large band gap material, such as InGaAs, is then deposited on top of the InAs epitaxial layer (Ustinov 2001). Through post-deposition heat treatment, quantum dots are formed by self-assembly.

Another method is a combination of electron beam lithography and MBE. The electron beam is used to etch a pattern onto the substrate, and then MBE is used to deposit quantum dot materials on top. Usually the pattern is an array of holes, and these holes act as preferential nucleation sites for dots. The cost is high, but the position of dots can be controlled (Atkinson 2006).

4.4 Applications for quantum dots

Semiconductor quantum dots can be tuned and adjusted for many applications, including optics, medicine, and quantum computation. Quantum dots are used in biolabeling, in anti-counterfeiting applications to create special inks, in dyes and paints, in light displays, and in chemical sensing (Rogers 2008).

4.4.1 Life science

Quantum dots have many applications in life science. Non-cadmium quantum dots can be used for in vivo imaging. Quantum dots preferentially stain the vascular and lymphatic system, tumors, etc. in large multicellular animals such as mice. Western blotting, cell staining, flow cytometry, and cellular uptake are other examples of quantum dot applications.

Cadmium telluride (CdTe) and CdSe nanocrystals are of great industrial interest for developing photoluminescence-based biomedical labeling reagents (Peng 2001). Figure 4.6

shows an application of non-cadmium quantum dots for life science: *in vivo* imaging with preferential staining in specific parts.

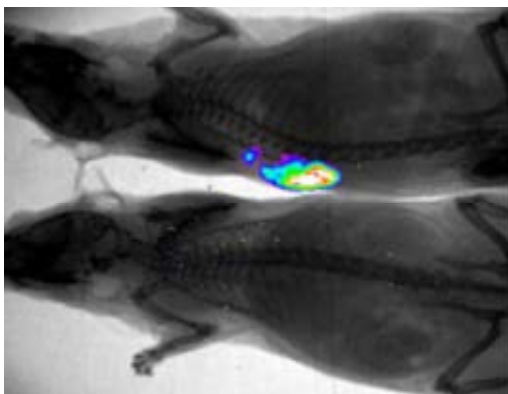


Figure 4.6 Quantum dots application for *in vivo* imaging (Evident).



Figure 4.7 Quantum dots application for display device (Evident).

4.4.2 Display

Quantum dots have applications in both organic and inorganic light emitter devices such as electroluminescence (EL) devices. They are dispersed within or between phosphor layers and emit a specific color of light. Quantum dots can be applied over large areas using liquid-phase deposition techniques such as roll-to-roll printing and spin coating. The emission colors of nanophosphors based on quantum dots can be tuned by changing the dot size (Sandia). Also, quantum dots are utilized to enhance light-emitting diodes (LEDs) and can emit almost any color (Evident). Figure 4.7 shows an application of quantum dots for a color display device.

4.4.3 Photovoltaic devices

Quantum dots can be tuned to desired sizes and band gaps. Using a single material, composed of different sizes of quantum dots, multiple band gaps are available. Different layers of different band gaps can then be used to reduce loss of incident light. Multiple band gaps can absorb photons from several different wavelengths according to their band gap energies. This allows increased photon-to-electron conversion efficiency in photovoltaic devices (Bukowski 2002). Also, quantum dots are cost-effective and can be incorporated into semiconductor polymers or inks and deposited onto low-cost substrate by roll-to-roll printing techniques (Evident).

4.4.4 Photonics and telecommunications

Quantum dots provide an attractive opportunity to develop optical switches, modulators, and other nonlinear optic devices. This is because quantum confinement enhances nonlinear absorption and nonlinear refractive index (Evident). Quantum dots can be used for optical switches and logic gates that work faster than 15 terabits per second. Another potential application is the quantum dot laser (Bukowski 2002; Grundmann 2000). The tunable band gap of quantum dots makes the laser wavelength changeable. Also, lasers with quantum dots have potential for very low-threshold current density, which is the current required to stimulate the laser or create output power from the device. InGaAs/AlGaAs, GaAs/InAs are the most studied material for the quantum dot laser. For laser application, single- or multi-quantum dot layers are used. Figure 4.8 shows the structure of a quantum dot laser with multiple active layers (Fujitsu).

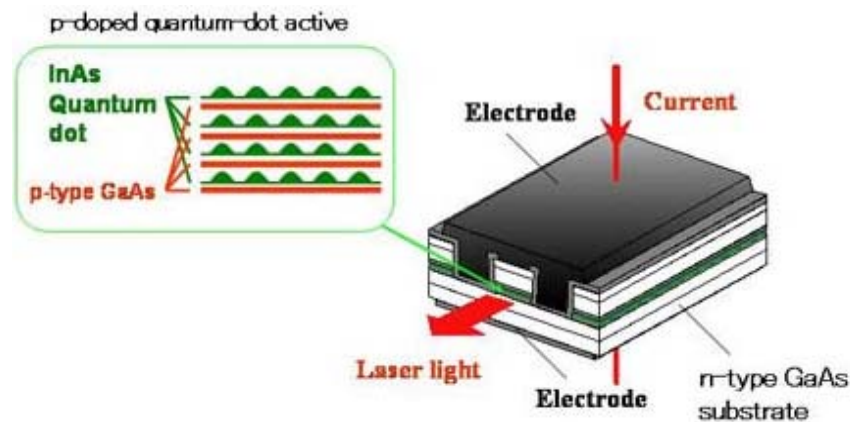


Figure 4.8 Structure of proposed quantum dot laser.

4.4.5 Security inks

For security and anti-counterfeiting applications, inks and paints incorporated with quantum dots can be applied to many types of surfaces, including papers, plastics, and metals. The wide range of color combinations of multiple quantum dots and other pigment create a unique visible image that identifies any subject or document when exposed to UV light (Evident; The Royal Society).

Figure 4.9 illustrates schematically the samples of info-inks⁷ consisting of three different quantum dots with different emission wavelengths. Adjusting the quantum dots can produce

⁷ Info-ink consists of CdSe quantum dots, toluene, and polystyrene.

a series of 3-digit codes (Chang 2004). Companies involved with quantum dots are listed in Appendix II.

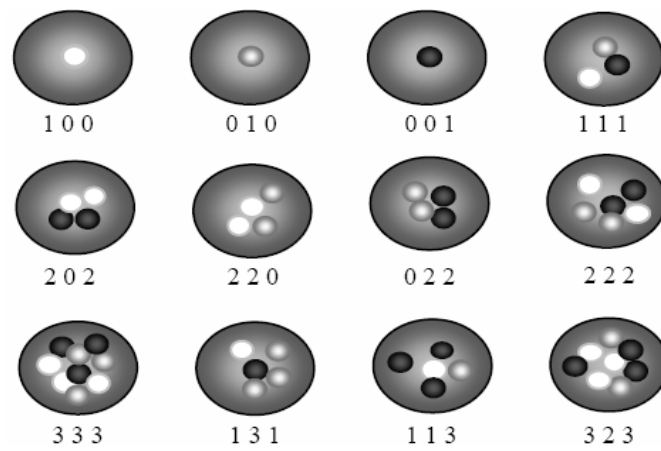


Figure 4.9 Information contained in info-ink using quantum dots (Chang 2004).

V. CATALYSTS IN NANOMATERIALS

Catalysts are widely used in the chemical and pharmaceutical industries. The use of nanoparticles enhances catalyst activity because of a large contact area between the active material of the catalyst and the surrounding materials. Generally, nanoparticles 1 to 10 nm in diameter are used for catalysts. As the size of the catalyst particles decreases, the ratio of surface area to volume increases and further enhances the catalytic activity. Thus, nanoparticles are one of the best materials for catalysts due to their very large surface-area-to-volume ratio.

5.1 Cerium oxide (CeO₂) nanoparticles

Oxides of rare earth elements have been used widely in the catalyst industry to improve activity, selectivity, and thermal stability. Cerium oxide is one of the most significant of these rare earth elements and has seen recent use as a combustion catalyst. The catalyst function of CeO₂ is related to its gas phase reaction with oxygen and ability to shift between the reduced and oxidized state, i.e., Ce³⁺ and Ce⁴⁺. This reversible reaction is expressed below (Masui 2000):



5.1.1 Fabrication of CeO₂

Low-temperature hydrothermal synthesis is one method of making nanocrystalline CeO₂ particles. Raw materials for this synthesis are cerium carbonate (Ce₂(CO₃)₃·3H₂O), hydrous cerium oxide, acetic acid (CH₃COOH), hydrogen peroxide (H₂O₂), nitrate acid (HNO₃), and ammonia hydroxide (NH₃). The specific procedure is explained below (Tok 2007).

When cerium (IV) hydroxide (Ce(OH)₄) is used as the precursor for CeO₂, cerium carbonate is first dissolved in nitric acid to yield cerium (III) nitrate. Cerium (III) nitrate, Ce(NO₃)₃·6H₂O, is diluted to [Ce⁴⁺] = 0.5M using D.I. water. Hydrogen peroxide in the molar ratio (H₂O₂: Ce⁴⁺) of 1:2 is added to cerium (III) nitrate solution and stirred for 5 minutes under heat to convert Ce³⁺ to Ce⁴⁺. Dilute ammonia solution (7M) is then added to the mixture until a pH of 8.8 is achieved. Upon adding ammonia solution, cerium (IV) hydroxide (Ce(OH)₄ or CeO₂ + 2H₂O) is precipitated with a light yellow color. The precipitate is washed with distilled water several times. The precipitates are then placed in an

oven to dehydrate (250°C for 6 hrs), and form CeO₂ particles. The dried powders are ground to a particle size of 5 to 6 nm.

5.1.2 Application as additive in diesel fuel

The most current interest is in treatment of exhaust emissions (Oxonica; Trovarelli 2001). CeO₂ can be used as a diesel fuel combustion catalyst to reduce fuel consumption, as well as CO₂ and other harmful exhaust emissions. A CeO₂-based diesel fuel catalyst is available commercially in Europe (Oxonica). Another potential application is the removal of organics from wastewater.

Diesel exhaust is a complex of gases, vapor, and fine particulates. The gaseous fraction includes air pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x), and volatile hydrocarbons (HC). The catalyst converts NO_x, HC, and CO in exhaust gases into innocuous nitrogen, carbon dioxide (CO₂), or water (H₂O).

During the auto exhaust treatment, CeO₂ nanoparticles act as an oxygen buffer to provide oxygen. CeO₂ nanoparticles have the ability to donate its oxygen for the removal of CO and hydrocarbon (HC) during oxygen-deficient conditions, while absorbing and storing oxygen from O₂, NO and water during oxygen-rich conditions (Tok 2007; Trovarelli 2001). Due to the large surface area, Ce₂O nanoparticles make a very effective catalyst and oxygen buffering agent. A cerium oxide/zirconium oxide (CeO₂-ZrO₂) system can be used to provide thermal stability and improve the efficiency of CeO₂ catalytic function (Colussi 2004). Companies involved with metal oxides catalysts are listed in Appendix II.

5.2 Gold (Au) nanoparticles

Although gold is viewed as an inert metal, gold nanoparticles less than 5 nm in diameter have been found to be catalytically active for several chemical reactions. Nano-size gold particles can be a very effective catalyst under mild conditions or less-than-ambient temperature. Operating at lower temperatures equates to lower chemical plant operation costs. Combined with other material such as titanium oxide (TiO₂), gold nanoparticle catalysts show high activity for oxidation of CO (Thompson 2007; Hvolbaek 2007, Ho 2007).

5.2.1 Fabrication methods for gold nanoparticles

One method of making gold nanoparticles is to reduce hydrogen tetrachloroaurate (HAuCl_4) in a boiling sodium citrate solution. Precipitated gold nanoparticles show a deep wine color. The average particle size range is 10 to 100 nm diameter and can be controlled by the concentration ratio of gold salt and sodium citrate (Marzan 2004).

Another method is the two-phase (water-toluene) reduction method. Gold tetrachloride (AuCl_4^-) is transferred from an aqueous solution to toluene using tetraoctylammonium bromide ($[\text{CH}_3(\text{CH}_2)_7]_4\text{NBr}$) as the phase-transfer reagent; it is reduced with aqueous sodium borohydride (NaBH_4).

Aqueous solution of HAuCl_4 is mixed with organic solution of tetraoctylammonium bromide in toluene. The two-phase mixture is stirred until all the tetrachloroaurate transfers into the organic layer. Dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{SH}$) is then added to the organic phase, and sodium borohydride is slowly added with vigorous stirring. After further stirring for 3 hours, the organic phase is separated. The solution is evaporated in a rotary evaporator, and then mixed with ethanol to remove excess thiol. The mixture is kept for 4 hours at -18°C , and the dark brown precipitate is filtered and washed with ethanol. The crude product is dissolved in toluene and again precipitated in ethanol (Brust 1994). Average particle size of gold is 1 to 10 nm (Marzan 2004). Figure 5.1 shows a flow diagram for gold synthesis with the two-phase reduction method.

Gold nanoparticles can also be made by the reduction of metal salts using an organic solvent. Ethanol has been long used for the preparation of metal nanoparticles such as platinum (Pt), palladium (Pd), gold (Au), or rhodium (Rh) in the presence of a protecting polymer, usually poly(vinyl pyrrolidone) (Marzan 2004). Other methods that can be used fabricate gold nanoparticles are physical vapor deposition (P&I) and chemical vapor deposition (Palgrave 2008).

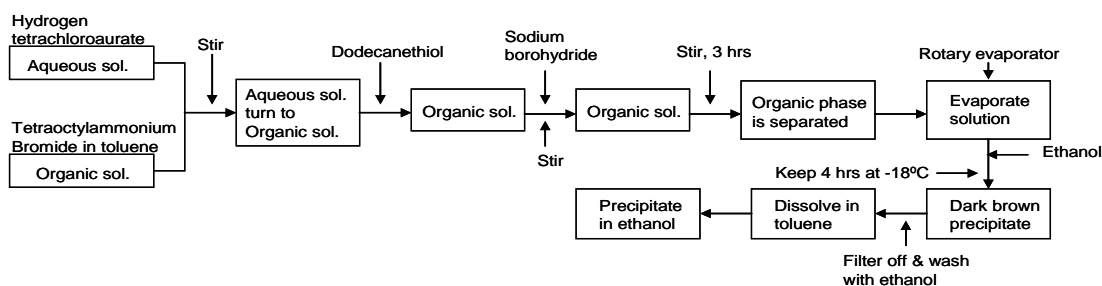


Figure 5.1 Process flow diagrams for gold precipitation with two-phase reduction method.

5.2.2 Applications of gold catalysts

The chemical activity of gold is changed with particle size. It is known that only gold nanoparticles less than 5 nm in diameter show catalytic activity. Small particles have a relatively large number of low-coordinated gold atoms, which are located at the edges and at the corners of particles⁸ (Hvolbaek 2007). Atoms on the corners and edges of gold nanoparticles are the active sites. Figure 5.2 shows a calculation of the fraction of atoms that are located at corners, on edges, or on the surface in the top half of a truncated octahedron as a function of the particle diameter.

The ratio of corner atoms to surface or edge atoms increases significantly when the particle size is less than 3 nm. The increase in the estimated ratio of corner atoms with decreasing gold particle size coincides with observed increase in CO oxidation activity. Thus, the total number of atoms located at the corners of the nanoparticles has a major influence on the activity of a gold catalyst (Janssens 2007).

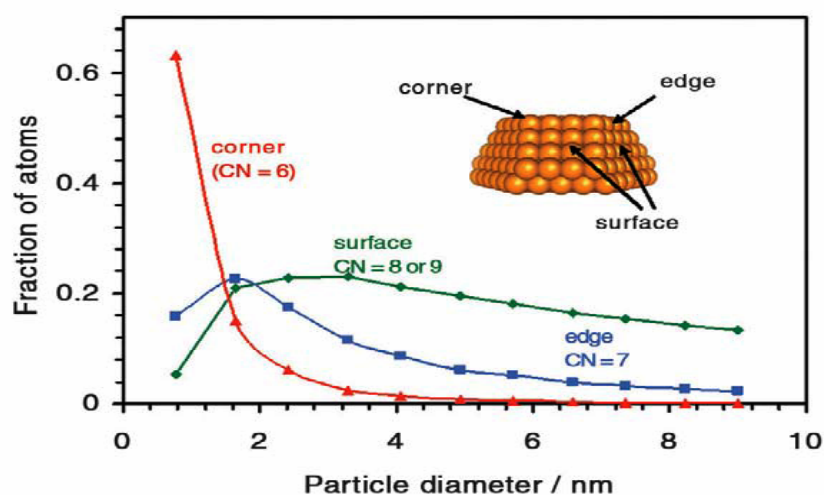


Figure 5.2 Calculated fractions of gold atoms at corners, edges, and particle surfaces in the top half of a truncated octahedron as a function of gold particle diameter. The insert shows a truncated octahedron and the position of representative corner, edge, and surface atoms (Janssens 2007).

Nanoparticle catalysts are active at or below ambient temperature, which makes them unique. The mild conditions under which the nanoparticle gold catalysts are active make

⁸ It is considered that these Au atoms with low-coordinated number are able to bind CO and O₂, which is prerequisite for a catalytic reaction.

them attractive for a number of applications. Table 5.1 shows potential applications of gold nanoparticles as catalysts.

Industry	Field	Purpose
Chemical processes	Oxidation of glucose to gluconic acid	Food additive and cleaning agent
	Production of methyl glycolate from ethylene glycol and methanol	Solvent for semiconductor manufacturing, cleaner for metals and boiler
	Manufacturing of vinyl acetate monomer (VAM)	Wood glue, wallpaper paste, emulsion-based paint
Pollution control	Air filter Catalytic converter	Oxidation of CO and nitrogen compound
	Water treatment	Treatment for hydrodechlorination of trichloroethene
Fuel cells	Production of hydrogen from CO and steam	Prevent poisoning the Pt by CO
Sensor	Gas sensor	Detecting CO, NO _x
	Color-change sensors	Monitoring components of body liquids

Table 5.1 Potential applications of gold nanoparticles as catalysts (modified from Thompson 2007).

5.2.3 Other properties of gold nanoparticles

Nanoparticles of some metals with free electrons (gold, silver, and copper) possess plasmon resonance in the visible spectrum, which gives rise to colors. Their optical properties depend on the particle size and shape. The electric field of the incoming electromagnetic radiation induces the formation of a dipole in the nanoparticle. A restoring force in the nanoparticles tries to compensate for this, resulting in a unique resonance wavelength, i.e., surface plasmon resonance. For example, bulk gold looks yellowish in reflected light, but thin gold films look blue in transmission. This characteristic blue color steadily changes to orange, purple, and red as the particle size is decreased to approximately 3 nm. (Marzan 2004).

VI. Silver (Ag) nanoparticles

Like gold nanoparticles, silver nanoparticles possess plasmon resonance in the visible spectrum, which gives rise to colors. This is due to the surface plasmon-oscillation mode of the conduction electrons that are coupled through the surface to the external electromagnetic field (Jacob 2007).

6.1 Fabrication of silver nanoparticles

Generally, silver nanoparticles are fabricated by a chemical colloidal process. A colloidal silver dispersion is prepared by the reduction of silver nitrate (AgNO_3) in ethylene glycol in the presence of a water-soluble polymeric protective agent, polyvinylpyrrolidone (PVP). For fabrication of silver nanoparticles, AgNO_3 , ethylene glycol (solvent), and polyvinylpyrrolidone (PVP) (reducing agent of AgNO_3) are used as the starting materials. PVP is dissolved into ethylene glycol, and AgNO_3 is added. The solution is heated up to 120°C and held at that temperature for 1 hour. After the solution is cooled to room temperature, acetone is added. The solution is then centrifuged to recover silver nanoparticles. The average particle size of recovered silver nanoparticles is 15 to 35 nm (Silvert 1996). Figure 6.1 illustrates processes for fabrication of silver nanoparticles.

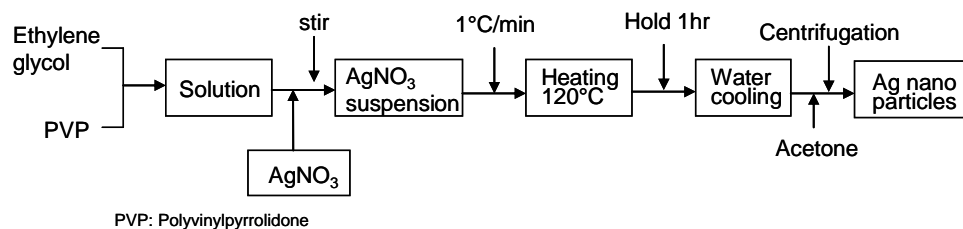


Figure 6.1 Process flow for fabrication of silver nanoparticles using the chemical colloidal method.

6.2 Applications of silver nanoparticles

As the size of silver particles decreases to the nano-scale, their antibacterial efficiency increases due to their large surface area per unit volume. Silver ions generated from the silver surface bind to the reactive group in the target cell or organism, resulting in their precipitation and inactivation. There are many types of products using silver antibacterial properties in the market (see Appendix I).

Paint mixed with silver nanoparticles shows excellent antimicrobial properties, as the nanoparticles kill both gram-positive and gram-negative pathogenic bacteria (Kumar 2008). Man-made and natural fibers can be enhanced with antibacterial properties via silver nanoparticles that are chemically and permanently bonded to the fibers. These silver-based antibacterial fibers can be used in a range of applications, from performance apparel to medical equipment. Silver nanoparticles can also be used as an additive for various polymer applications such as PET, PP, PE, and other polymers (NanoHorizons). Figure 6.2 shows one example of silver particles on fiber.

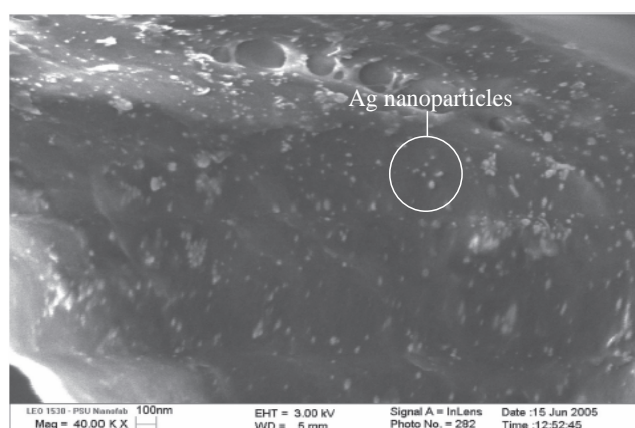


Figure 6.2 Transmission electronic microscopy image of silver nanoparticles on fiber (NanoHorizons).

Silver nanoparticles are also used in filters for air conditioning, washing machines, and refrigerators (Gleiche 2006). Silver nanoparticles, combined with TiO_2 nanoparticles, can be used to enhance antibacterial, deodorizing, and photocatalytic effects of TiO_2 (Three-bond chemicals).

VII. Titanium dioxide (TiO₂) nanomaterials

Traditionally, titanium dioxide materials have been used as a white pigment in paint, and the paint industry has been the largest consumer. With development of TiO₂ nanomaterials, applications have greatly expanded to other areas, such as cosmetics, energy, and photocatalysts. TiO₂ nanomaterials have applications in diverse areas, including ultraviolet protection, photocatalysts, photovoltaics, sensing, water treatment, antibacterial agents in medical devices, pigments, and air purification. Sol-gel and hydrolysis processes are used to synthesize TiO₂ nanoparticles using titanium tetrachloride (TiCl₄) as the raw material.

Titanium dioxide has a large band gap energy, more than 3.0 eV, and relatively long electron-hole pair recombination time. These properties allow use of TiO₂ nanoparticles for many different applications. The photocatalytic reaction of TiO₂ is very effective at decomposing organic matter. This property is used for self-cleaning products such as coating for exterior walls and windows. Usage of nano-size TiO₂ particles for antibacterial action ranges widely from interior tiles to computer peripherals (Iogear; Fujishima 1999). The large band gap property of TiO₂ provides UV protection in sunscreen products. TiO₂ nanoparticles absorb harmful ultraviolet radiation and are transparent to visible light when less than 50 nm in diameter. In a solar water-splitting system and in solar cells, TiO₂ nanoparticles are used as the electrode and electron acceptor, respectively (Takabayashi 2004; Bjorklund 2007). Companies involved with metal oxide catalysts are listed in Appendix II.

VIII. Other nanomaterials

8.1 Nano-ink

Dip-Pen nanotechnology (DPN) is a process for deposition of nanomaterial in the form of ink onto a substrate. Scanning-probe microscopy tips or hollow tips can be used for deposition. The major application is patterning with an atomic-force microscopy tip. Schematic descriptions of DPN are shown in Figure 8.1. DPN can be used to deposit multiple compounds, sequentially or in parallel, and is a direct-write lithographic tool that allows soft and hard materials to be printed from scanning probe tips onto a surface with high resolution of sub-50 nm (Salaita 2007; Ginger 2004).

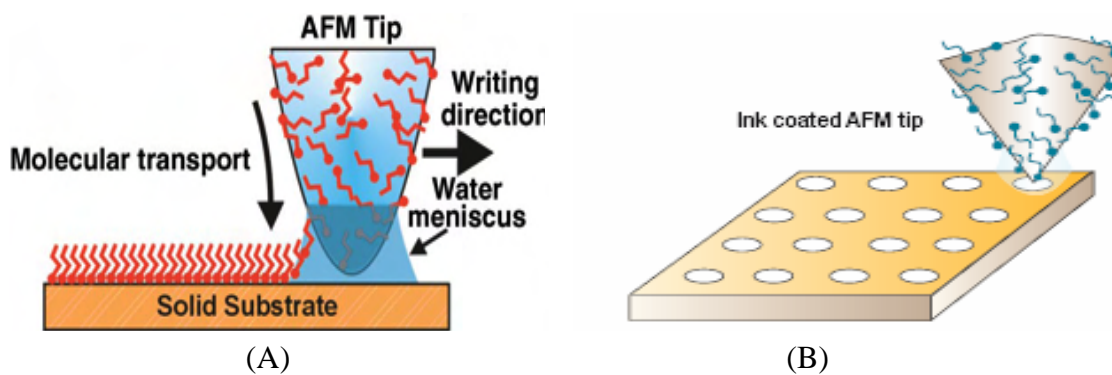


Figure 8.1 Schematic representation of the DPN process. (A): A water meniscus forms between the AFM tip, which is coated with “ink” molecules and the solid substrate. (B): Generation of nano-array with AFM tip on gold substrate.

DPN can be used in biological templates. Antibody nanoarrays can be fabricated using DPN-patterned dot features as templates for antibody immobilization. DPN is used for DNA arrays for molecular electronics, solid-state etch resist templates, and electromechanical patterning (Nanoink; Salaita 2007; Ginger 2004). Also, DPN can be used for patterning on metal surfaces, insulators, and functional layers on a variety of surfaces. Thiols, proteins, and dyes can be used for ink, and gold, silicon dioxide (SiO_2), and silicon (Si) are used for substrate (Ginger 2004).

8.2 Nano-lubrication materials

The tribological phenomena of adhesion, friction, and wear arise when solid objects make contact. As the size of devices shrinks to micro- and nanoscale, the surface-to-volume ratio increases and the effect of body forces (gravity and inertia) becomes insignificant compared

to those of surface forces such as van der Waals, capillary, electrostatic, and chemical bonding (Kim 2007).

As a result, tribological behavior of contacts in small scale differs from those in a macroscopic engineering structure. Also, at the micro- and nanoscale, adhesion becomes significant. Thus, conventional lubrication methods cannot be applied directly to micro- and nanoscale devices. New nano-engineering approaches must be employed for nano-size devices with moving structure.

Nanospheres of inorganic materials could be used as lubricants by acting as nano-size ball bearings. Nanoparticles reduce friction between metal surfaces, particularly at high normal load (The Royal Society). One possible method of nano-lubrication is coating with hard materials. Coating with strong, wear-resistant materials can reduce friction and wear on silicon-based devices. For example, diamond-like carbon (DLC) is already used in magnetic hard disk storage systems (Kim 2007).

IX. NANOTECHNOLOGY IN CONSUMER PRODUCTS

There are many consumer products using nanotechnology on the market. But nanotechnology or nanomaterials in these products are not easy to recognize. Because nanomaterials are embedded into other materials or used in very small amounts, consumers may not be aware of their presence. In this chapter, products are categorized into 9 industries: appliances, automotive, food and beverage, electronics, textiles, home and garden, sports, cosmetics, and other industry.

A total of 175 types of products⁹ are identified in 9 different industries, based on the Woodrow Wilson Center inventory list (WWC). Silver nanoparticles are the most frequently used nanomaterials. Silver's antibacterial function is a well-known property. The ease of application (simply coating the product surface) has popularized its use. Use of silver nanoparticles is identified in 6 of the 9 industries, and it is expected in the near future in the automotive and sports industries.

The primary nanomaterials are carbon nanotubes for the sports and electronics industries, and nanoclays and carbon nanotubes for the automotive industry. Carbon nanotube technology has yet to be applied to other industries, but composite materials utilizing carbon nanotubes have been widely used in both the sports and automotive industries. For the sports industry, the main functions are light weight and structural strength of material. For the automotive industry, the main functions are light weight, anti-static properties, and electrical conductivity. In the electronic industry, carbon nanotubes are used for conductive transparent film and heat transfer. Potentially, they could be used as an electron emitter for displays and channel material for transistors.

The photocatalytic function of TiO₂ nanoparticles is used in self-cleaning and antibacterial products, while the high band gap energy property of TiO₂ nanoparticles is used in UV protection products. Other functions that nanotechnology consumer products provide include stain resistance, deodorizing, surface protection, and moisture control. Table 9.1 summarizes the major nanomaterials, technologies, functions, and number of product types

⁹ One product type can include many different individual products. For example, sunscreen in the cosmetic industry includes many different single products from many companies with different brand names. Thus, if every individual product were counted, the number of products is much larger than 175.

in each industry. For details, see Appendix I¹⁰, Nanotechnologies in Consumer Products Inventory List.

Industry	Major materials	Major technologies	Major functions	# of Product types
Appliance	Ag	Coating*	Antibacterial	11
Automotive	Clay, CNT	Coating, Composite	Lightweight, conductive	18
Food and Beverage	Ag	Coating*	Antibacterial	16
Cosmetics	Ag	Particle	Antibacterial, Moisture control	17
Home and Garden	Ag, TiO ₂	Coating*	Antibacterial, Self-cleaning	47
Sports	CNT	Composite	Lightweight, strong	17
Electronics	CNT, Ag	Coating, Composite	Conductive, Antibacterial	16
Textile	Ag	Coating*	Antibacterial	21
Other	TiO ₂ , Ag	-	Self-cleaning	12

Table 9.1 Summary of major nanomaterials, technologies, and functions, and number of product types in each industry. *: The technology is not clearly identified. -: Information is not available.

¹⁰ For this inventory list, the Woodrow Wilson Center nanotechnology consumer products inventory list and other sources were utilized.

SUMMARY

Nanotechnology refers to a wide range of technologies involving materials with at least one dimension between approximately 1 and 100 nanometers. Such applications exploit the properties, distinct from bulk/macroscale systems, of nanoscale components.

In nanometer range, particles exhibit different mechanical, thermal, optical, and electrical properties from the bulk material. Large surface area to volume ratio provides various new and unique properties, which are utilized in many fields of nanotechnology such as composites, electronics, and chemical sectors. Quantum dots are an example of novel properties offered through nanotechnology. In quantum dots, quantum effects at the nanoscale restrict electron-state density in a discrete manner. This property enables quantum dots to emit different colors according to their specific particle size when stimulated with sunlight, thermal energy, electricity, or other forms of energy.

The concept of nanotechnology was introduced in 1959 in physicist Richard Feynman's talk "There's Plenty of Room at the Bottom." In 1991, Sumio Iijima discovered carbon nanotubes, which are tube-shaped materials whose diameter measures on the nanometer scale. Carbon nanotubes show a very high aspect ratio, which plays a great role in their many applications. Nanotechnology is being developed with characterization tools such as atomic force microscopy (AFM), scanning and/or tunneling electronic microscopy (SEM, TEM), and synthesis methods such as sol-gel, chemical vapor deposition (CVD), and arc discharge.

Carbon-based nanomaterials include carbon nanotubes, fullerenes, carbon nanofibers, carbon black, and carbon onions. Carbon nanotubes have a diameter as small as 1 nm and a length of a few nanometers to a micron. Carbon nanotubes are the most intensively researched nanomaterial and have great potential for numerous applications. Carbon nanotubes are used in the plastics industry for composite materials, the electronics industry for display or conductive transparent films, the semiconductor industry for transistor channels, the energy industry for batteries or solar cells, and the bio-health industry for sensors.

Fullerenes are used for cosmetics, and carbon onions can be used for solid lubrication. The primary use of carbon black is in rubber products, mainly tires and other automotive rubber products. Carbon nanofibers are used as filler for composite materials.

Unlike conventional standard fillers, nanocomposite filler is needed only in very small amounts (less than 5 wt%) to greatly improve mechanical, thermal, and electrical properties. Furthermore, all of these benefits are available without sacrifices in density of the composite or light transmission of matrix resins.

Current major applications of plastic nanocomposite materials are automotive parts, sporting goods, and packaging. Nylon and nanoclay are used in combination for barrier layers in multilayer polyethylene terephthalate (PET) bottle and films for food packaging. Nanoclay is used to increase structural hardness in plastic polymer nanocomposite materials because of its relative low cost compared to carbon nanotubes.

Emission color from a quantum dot depends on the size of the quantum dots. The smaller quantum dots have larger band gap energy. Thus, by simply altering the size of materials, we can change the band gap energy and the color of light emitted. There are several methods for fabrication of quantum dots: molecular beam epitaxy (MBE), e-beam lithography, metal organic chemical vapor deposition (MOCVD), and colloidal synthesis. These semiconductor quantum dots are used in biolabeling; anti-counterfeiting applications to create special inks, dyes and paints; light displays; and chemical sensing. Non-cadmium quantum dots can be used for in vivo imaging.

Gold nanoparticles less than 5 nm in diameter are catalytically active for several chemical reactions. Nano-size gold particles are very effective catalysts under ambient temperature. Lower process temperatures result in lower chemical plant operation costs. Additionally, gold nanoparticle catalysts combined with other material such as Au/TiO₂, show high activity for oxidation of carbon monoxide.

CeO₂ can be used as a diesel fuel combustion catalyst, which reduces fuel consumption, CO₂ emission, and other harmful exhaust emissions. Treatment of exhaust emissions has been the primary focus to date, although another potential application is removal of organics from wastewater.

Silver ions generated from silver surfaces bind to a reactive group in target cell or organisms, resulting in their precipitation and inactivation. There are many types of products on the market that utilize the antibacterial properties. Silver-based antibacterial fibers are used in products ranging from performance apparel to medical equipment.

Titanium dioxide nanoparticles have a large band gap and are used for ultraviolet (UV) protection, photocatalysts, photovoltaics, and sensing. As a photocatalyst, TiO₂ nanomaterial is being applied to exterior walls of buildings to provide a self-cleaning function.

Many nanotechnology-based consumer products have emerged on the marketplace. A total of 175 types of products are identified in 9 different industries. Silver nanoparticles have been identified as the most frequently used nanotechnology. The ease of application (simply coating the product with silver nanoparticles) for antibacterial function has popularized its use in 6 industries. The primary nanomaterials are CNTs for the sports and electronics industries, and CNTs and clays for the automotive industry. Compositing is the major technology for CNTs in both sports and automotive industries. Other industries were not found to use CNTs.

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APPENDIX

Appendix I: Nanotechnologies in consumer products

Appendix II: Companies list in nanotechnology

Appendix I: Nanotechnologies in Consumer Products

1. Electronic products

#	Product	Technology	Material	Function
1	Camera image sensor	-	-	-
2	Camera lenses	coating	-	Anti-reflective
3	Cell phone surface	coating	Ag	Antibacterial
4	Computer	-	Ag	Antibacterial
5	Computer main chip	etching, coating	-	-
6	Computer memory	etching, coating	-	-
7	Computer cooling fan	coating	CNT	-
8	Conducting film	composite	CNT	-
9	Display protection	coating	-	Surface protect
10	Electron emitter	-	CNT	-
11	Guitar string	coating	-	-
12	Hard disk drive	etching, coating	-	-
13	Hearing aid	coating	-	Anti-adherent
14	Image sensor	etching, coating	-	-
15	Mouse, key board	coating	TiO ₂ , Ag	Antibacterial
16	Photo paper	coating	-	Durability

-: information is not available

2. Automobile products

#	Product	Technology	Material	Function
1	Air filter	nanofiber	-	-
2	Body side molding	composite	Clay	-
3	Cargo bed	composite	Clay	lighter, protect
4	Cylinder head gasket	particle	-	sealing
5	Engine oil additive	particle	Au	-
6	Exhauster catalyst	-	Palladium	longer life
7	Fuel additive	particle	CeO ₂	fuel efficiency
8	Fuel system	composite	CNT	anti-static
9	Motor oil filter	fiber	-	-
10	Paint additive	coating	CNT	lighter, protect
11	Road safety glow	-	-	-
12	Side view mirrors	coating	TiO ₂	Self-cleaning
13	Surface treatment	coating	-	Anti-scratch
14	Tire additive	particle	Si, C-black	-
15	Wheel rim cleaner	coating	-	cleaning
16	Window cleaning	particle	-	-
17	Window sunscreen	coating	TiO ₂	UV filter
18	Electric car battery	particle	TiO ₂	-

-: information is not available

3. Food and beverage products

#	Product	Technology	Material	Function
1	Bottle brush	particle	Ag	Antibacterial
2	Chopstick	particle	Ag	Antibacterial
3	Cup	particle	Ag	Antibacterial
4	Cutting board	particle	Ag	Antibacterial
5	Food container	particle	Ag	Antibacterial
6	Kitchenware	particle	Ag	Antibacterial
7	Oil	particle	-	-
8	Pacifier	particle	Ag	Anti-bacterial
9	Plastic beer bottle	composite	Clay	Barrier
10	Plastic storage bag	particle	Ag	Antibacterial
11	Plastic wrap	catalysis	ZnO	-
12	Silver liquid	-	Ag	-
13	Supplement	particle	Au, Pd, Ag	Cu, Ti, Ca
14	Tableware	particle	Ag	Antibacterial
15	Teapot	particle	Ag	Antibacterial
16	Wet wipe	particle	Ag	Antibacterial

-: information is not available

4. Cosmetic products

#	Product	Technology	Material	Function
1	Al powder	particle	Al	-
2	Cleaner	particle	Ag	-
3	Conditioner	-	-	-
4	Eye cream	-	-	Moisture ctrl.
5	Facial creams	particle	C ₆₀	Moisture ctrl.
6	Facial spray	particle	Cu	-
7	Fullerene powder	-	C ₆₀	-
8	Hair treatment	-	-	-
9	Hand cream	-	-	Moisture ctrl.
10	Lipstick	particle	ZnO	-
11	Lotion	-	-	Moisture ctrl.
12	Mask pack	particle	Au	-
13	Shampoo	particle	Ag	Antibacterial
14	Skin renewal	-	-	Moisture ctrl.
15	Soap	particle	Au	-
16	Sunscreen	particle	TiO ₂ , ZnO	UV protection
17	Toothpaste	particle	Ag	Antibacterial

-: information is not available

5. Textile products

#	Product	Technology	Material	Function
1	Blanket	-	Ag	Antibacterial
2	Elbow, knee guard	Particle coating	-	Antibacterial
3	Fabric softener	Particle	Ag	Antibacterial
4	Face mask	-	Ag	Antibacterial
5	Full body suit	-	-	Heat shield
6	Glove	-	-	-
7	Hat	-	-	-
8	Jacket	-	-	Retain dirt
9	Luggage bag	-	-	Stain resistance
10	Mask	-	-	Air filter
11	Mat	fiber	-	Antibacterial
12	Necktie	-	Ag	Antibacterial
13	Pants	-	-	Moisture mgmt
14	Pillow	Particle coating	Ag	Antibacterial
15	Shirt	-	-	Antibacterial
16	Shoe pad	-	-	Antibacterial
17	Sleeves & brace	-	Ag	Antibacterial
18	Slipper	-	Ag	Antibacterial
19	Socks	Particle coating	Ag	Antibacterial
20	Towel	-	-	-
21	Water short	-	-	UV protect

-: information is not available

6. Appliance products

#	Product	Technology	Material	Function
1	Air conditioner	filter	Ag	Antibacterial
2	Air purifier	filter	TiO ₂	Antibacterial
3	Audio cable	-	C	-
4	Battery	nanoparticle	phosphate	-
5	Fuel cell	catalyst	-	-
6	Humidifier	coating	Ag	Antibacterial
7	Power tool battery	particle	TiO ₂	-
8	Refrigerator	coating, insulation	Ag	Antibacterial
9	Shaver	-	Ag	Antibacterial
10	Vacuum cleaner	coating	Ag	Antibacterial
11	Washing machine	coating	Ag	Antibacterial

-: information is not available

7. Home and gardening products

#	Product	Technology	Material	Function
1	Air spray	particle	Ag	Antibacterial
2	Artificial teeth cleaner	particle	Ag	Antibacterial
3	Bed mattress	-	-	Moisture control
4	Bottle brush	-	Ag	-
5	Chopstick	-	Ag	Antibacterial
6	Cigarette filter	fiber	-	Filtration
7	Cushion	-	-	Stain resistance
8	Degreaser	-	-	-
9	Deodorant	-	ZnO	-
10	Door lock	coating	Ag	Antibacterial
11	Epoxy coating	coating	-	Protection
12	Fish tank cleaner	-	-	Antibacterial
13	Floor cleaner	-	-	-
14	Glue	-	-	-
15	Grooming kit	-	-	Antibacterial
16	Hairbrush	particle	Ag	Antibacterial
17	Hair iron	coating	Ag	Antibacterial
18	Handler	coating	Ag	Antibacterial
19	Lens cleaner	coating	-	Prot. & clean.
20	Lubricant	coating, particle	inorganic	Lubrication
21	Makeup tool	coating	Ag	Antibacterial
22	Mosquito repellent	particle	-	-
23	Nail moisturizing	-	ZnO	-
24	Paint additive	coating	-	Antibacterial
25	Paper coating	coating	-	Prot. & clean.
26	Pet products	coating	Ag	Antibacterial
27	Photocatalyst spray	-	-	-
28	Respirator	-	Ag	Antibacterial
29	Self-cleaning window	coating	TiO ₂	Self-cleaning
30	Shoe-cleaning kit	-	Ag	-
31	Sticker	-	-	Deodorizing
32	Thermal patch	-	-	Antibacterial
33	Toilet	-	-	-
34	Toothbrush	particle	Ag	Antibacterial
35	Tooth developer	-	Ag	Antibacterial
36	Toy	particle	Ag	Antibacterial
37	Umbrella	-	-	Moist control
38	Watch chain	coating	Ag	Antibacterial
39	Water filter	membrane	-	-
40	Water tap	coating	Ag	Antibacterial
41	Wet wipes	-	Ag	Antibacterial
42	Wood coater	coating	-	Protection
43	Outside wall paint	coating	TiO ₂	Self-cleaning
44	Mirrors	coating	TiO ₂	Self-cleaning
45	Building glasses	coating	TiO ₂	Self-cleaning
46	Interior tiles	coating	TiO ₂	Self-cleaning
47	Exterior tiles	coating	TiO ₂	Self-cleaning

-: information is not available

8. Sports products

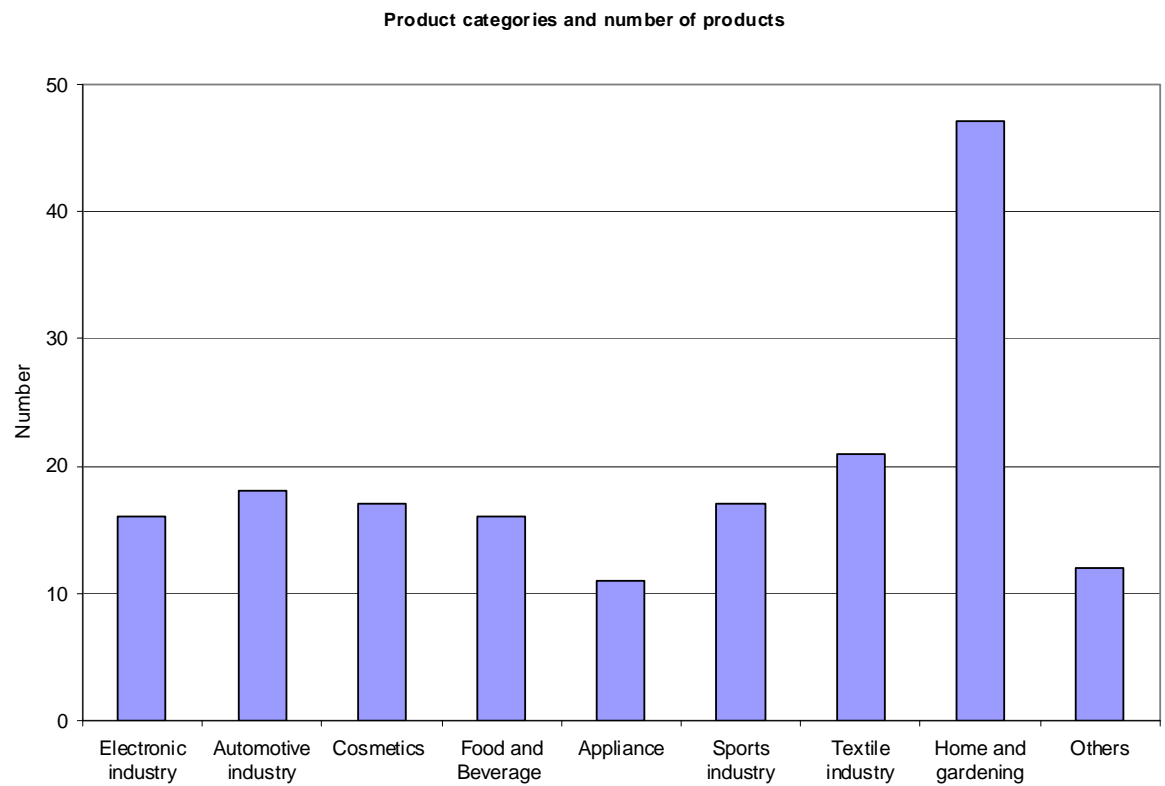
#	Product	Technology	Material	Function
1	Badminton racket	composite	SiO ₂	Lightweight, strong
2	Baseball bat	composite	CNT	Lightweight, strong
3	Bicycle frame	composite	CNT	Lightweight, strong
4	Bowling ball	composite	-	-
5	Crampon	composite	-	Lightweight, strong
6	Fishing lures	coating	-	-
7	Fishing rods	composite	Ti	Lightweight, strong
8	Fog eliminator	coating	-	Cleaning
9	Golf ball	composite	-	-
10	Golf shaft	composite	-	Lightweight, strong
11	Hockey sticks	composite	CNT	Lightweight, strong
12	Ice ax	alloy	Fe-Al	Lightweight, strong
13	Ski	particle	SiO ₂	Lightweight, strong
14	Ski wax	coating	-	Water-repellent
15	Snowboard	-	-	-
16	Tennis ball	composite	-	Lightweight, strong
17	Tennis racket	composite	CNT	Lightweight, strong

∴ information is not available

9. Other products

#	Product	Technology	Material	Function
1	Chem.haz.res.sys	-	-	-
2	Condom	-	Ag	Antibacterial
3	Metal alloy	-	-	lightweight
4	Pain relief cream	-	-	-
5	Pencil lead	-	-	-
6	Pregnancy tester	particle	Au	color change
7	Vaccine adjuvant	particle	CaP	Drug delivery
8	Wound dressing	particle	Ag	Antibacterial
9	Roofing	coating	TiO ₂	self-cleaning
10	Tents	coating	TiO ₂	self-cleaning
11	Road soundproof walls	coating	TiO ₂	self-cleaning
12	Road mirrors	coating	TiO ₂	self-cleaning

∴ information is not available



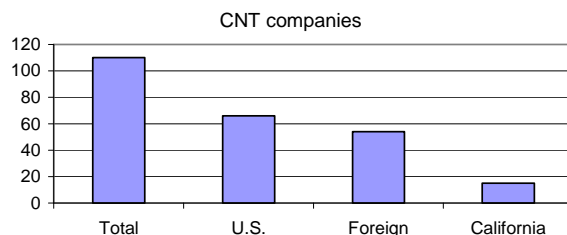
Appendix II: Companies in nanotechnology

1. Carbon nanotube companies list

	Company name	Products	Location	Web sites
1	Advanced nanopower	MW	Taiwan	www.anp.com.tw/English/main01.htm
2	Ahwahnee, Inc	MW	CA	http://www.ahwahneetech.com/
3	Alfa Aesar	MW	MA	www.alfa.com
4	AlphaNano technology	SW, MW	CHI	www.nanotubes.cn/index-en.htm
5	American Elements	SW, MW	CA	http://www.americanelements.com/
6	ApNano materials	CNT	NY	www.apnano.com
7	Apex Nanomaterials	SW, MW	CA	http://www.apexnanomaterials.com/
8	Applied nanotech	CNT	TX	www.appliednanotech.net
9	Applied science	CN Fiber	OH	http://www.apsci.com/home.html
10	Arkema	MW	FRA	http://www.arkema-inc.com/index.cfm
11	ARRY international	SW, MW	Hong Kong	www.array-nano.com
12	BASF	MW	GER	www.plasticspotal.com/products/ultraform.html
13	Bayer MateScience	MW	GER	http://www.baytubes.com/
14	Bio-nano international	CNT	Singapore	www.bionano.com.sg
15	Biophan	CNT	NY	www.biophan.com
16	BuckyUSA	SW, MW	TX	http://buckyusa.com
17	Buhler Partech	-	GER	www.buhlergroup.com
18	Canatu	CNT	Finland	www.canatu.com
19	CarboLex, Inc.	SW	PA	http://carbolex.com/
20	Carbon design innovation	CNT tip	CA	www.carbondesigninnovations.com
21	Carbon nanomaterial technology	SW, MW	KOR	www.carbonnano.co.kr/english.htm
22	Carbon nanotube and fiber 21	SW, MW	Austria	www.carbon-nanofiber.com
23	Carbon NT&F21	CNT, CNF	Australia	www.carbon-nanofiber.com
24	Carbon Solutions	SW	CA	http://www.carbonsolution.com/
25	Catalytic materials	MW	NC	www.catalysticmaterials.com
26	Cheap Tubes, Inc.	SW, MW	VT	http://www.cheaptubesinc.com/
27	Chengdo organic chemicals	CNT	CHI	www.timesnano.com
28	Cnano	SW, MW	CA	http://www.cnanotechnology.com/
29	Cnanz	CNT	NC	http://cnanz.com/index.html
30	C-polymers	CNT, CNF	Austria	www.c-polymers.com
31	Dupont	CNT	DE	www.dupont.com
32	E-City Nano Technologies	SW	MD	http://www.ecitynanotech.com/
33	eikos	-	MA	www.eikos.com
34	Electrovac	CNF	Austria	www.electrovac.com
35	Fujitsu laboratories	CNT	JPN	jp.fujitsu.com/group/labs/en
36	Future carbon GmbH	MW	GER	www.future-carbon.de
37	Graphene Solutions	-	WI	http://www.graphenesolutions.com/home
38	Hanwha chemical	SW, MW	KOR	http://hcc.hanwha.co.kr/English/index.html
39	HeJi	SW, MW	CHI	www.nanotubes.eu.com
40	Helix material solution	SW, MW	TX	www.helixmaterial.com
41	Hodogaya chemicals	-	JPN	www.hodogaya.co.jp/English2/web/
42	Honjo chemical	CNT	JPN	www.honjo-chem.co.jp
43	Hyperion catalyst	MW	MA	www.fibrils.com
44	IBM	CNT	NY	www.research.ibm.com/Nanoscience/nanotubes.html
45	Innovations unified technologies	CNT	India	www.iutechnologies.com
46	Ionic Liquid technologies	SW, MW	GER	www.nanomaterials.iolitec.de
47	Liftport	-	NJ	www.liftport.com/nanotech.htm
48	Lockheed Martin	CNT	CA	http://www.lockheedmartin.com/
49	MER corporation	-	AZ	www.opus1.com/~mercorp/index.htm
50	MicroTechNano	SW, MW	IN	http://www.microtechnano.com/
51	Mitsui	-	JPN	http://mitsuichemicals.com
52	MK nano	SW, MW	Canada	www.mknano.com
53	Molecular Nanosystems Inc	-	CA	http://www.monano.com/
54	mPhase technologies	CNT	NJ	www.mphase.com
55	MysticMD	CNT	CT	www.mysticmd.com
56	Nanergy	CNT	NJ	www.nanergyinc.com
57	Nano Factor Materials Tech.	SW, MW	IND	www.nanofactortubes.com
58	Nano NB	SW, MW	Canada	www.nanonb.com
59	NanoRidge	CNTcomp	TX	http://www.nanoridge.com/index.html
60	Nanostructure & Amorphous	SW, MW	TX	www.nanoamor.com
61	Nano-C	SW	MA	www.nano-C.com

61	Nanocarb lab	SW	Russia	www.nanocarblab.com
62	Nanocomp Technologies	-	NH	http://www.nanocomptech.com/
63	Nanocomposites	CNT	TX	www.nanocompositesinc.com
64	NanoCompound	MW	GER	www.nanocompound.de
65	NanoCS	SW, MW	NY	www.nanocs.com
66	Nanocyl	SW, MW	GA	www.nanocyl.com
67	NanoIntegris	SW	IL	http://www.nanointegris.com/
68	Nano-lab	SW, MW	MA	www.nano-lab.com
69	nanoleedge	CNT	CNA	www.nanoleedge.com
70	NanoMas technologies	CNT	NY	www.nanomastech.com
71	Nanomaterials research unit	SW, MW	Thailand	http://physcis.science.cmu.ac.th/nano
72	Nanomix Inc	-	CA	http://www.nano.com/
73	Nanoselect	CNT	DE	www.nanoselect-sensors.com
74	Nanoshel	CNT	India	www.nanoshel.com
75	Nanotailor	SW	TX	http://www.nanotailor.com/
76	NanotechLabs	CNT	NC	www.nanotechlabs.com
77	Nanothinx	SW, MW	Greece	www.nanotubesx.com
78	Nantero	CNT	MA	www.nantero.com
79	Natural nano	-	NY	www.naturalnano.com
80	N-tech	CNT	Norway	www.n-tech.no
81	NTP	SW, MW	CHI	www.nanotubes.com.cn
82	Optomec	CNT	NM	www.optomec.com
83	PlasmaChem	MW	GER	www.plasmachem.de
84	Polytech & Net	MW	GER	www.polytech-net.de
85	Porifera	CNT membrane	CA	http://poriferanano.com/
86	Pyrograph Products	CNF	OH	http://www.apsci.com/ppi-markets.html
87	Raymor nanotech	SW	Canada	www.raymor-nanotech.com
88	Rosseter Holdings	SW, MW	Cyprus	www.e-nanoscience.com
89	Samsung electronics	CNT	KOR	www.samsungelectronics.com
90	SELAH technologies	SW	SC	www.sealtechnologies.com
91	Seldon laboratories	CNT	Vermont	www.seldontechnologies.com
92	SES research	SW, MW	TX	www.sesres.com
93	Shenzhen nanotechnologies	CNT	CHI	www.nanotubes.com.cn
94	Showa Denko	CNT	JPN	http://www.sdk.co.jp/html/english/index.html
95	Smart Nanomaterials	SWCNT	TX	http://www.smartnanomaterials.com/
96	Solarno	CNT	TX	www.solarno.com
97	SouthWest NanoTechnologies,	SW	OK	http://www.swnano.com/index.php
98	Stanford Materials	SW, MW	CA	http://www.stanfordmaterials.com/
99	Sun nano	SW, MW	CA	www.nanomaterialstore.com
100	Sun nanotech Co.	MW	CHI	www.sunnano.com
101	ST microelectronics	CNT	Swiss	www.st.com
102	Surrey nanosystem	CNT	UK	www.surreynanosystems.com
103	Teco Nanotech	MW	Taiwan	www.teconano.com.tw
104	Thomas-Swan	SW, MW	UK	www.thomas-swan.co.uk
105	Tokyo chemical industry	CNT	JPN	www.tci-asiapacific.com
106	Unidym, Inc	SW, MW	CA	http://www.unidym.com/
107	Vorbeck materials	CNT	MD	http://www.vorbeck.com/
108	Xintek	MW	NC	www.xintek.com
109	YTC america	CNT	CA	www.ytca.com/carbon_nanotubes
110	Zyvex	MW	TX	www.zyvexpro.com

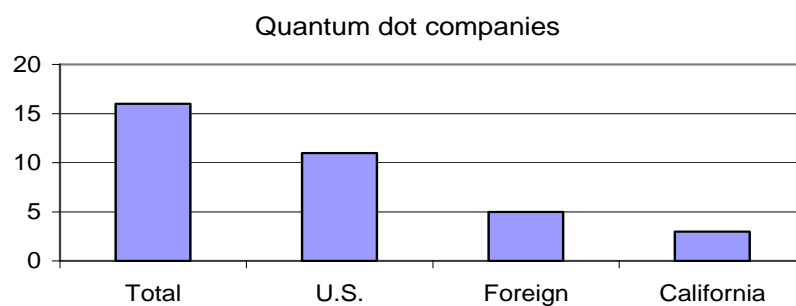
- -: information is not available
- Total: 110 companies
- US companies: 66, CA: 15
- Foreign companies: 54
- CNF: carbon nanofiber
- SW: single-walled
- MW: multi-walled



2. Quantum dots companies list

	Name	Products	Location	Web sites
1	American Elements	CdSe, CdTe, CdSe/ZnS	CA	www.americanelements.com
2	Antibody Incorporated	-	CA	www.antibodyinc.com
3	Evident Technologies	CdSe/ZnS, PbS	NY	www.evidenttech.com
4	Luna Nanoworks	Gd based QDs	VA	www.lunananoworks.com
5	MK Nano	CdSe, CdS, CdTe/CdS, CdTe	Canada	www.mknano.com
6	Nano Fluorescent Materials	CdGe/ZnS	Ukraine	www.nanofm.com
7	Nanoco Technology	CdSe, CdS	UK	www.nanocotechnologies.com
8	Nanosys	CdS, SiGe	CA	http://www.nanosysinc.com/
9	NN-Labs	CdSe/ZnS, CdS, CdSe	AR	www.nn-labs.com
10	Northern Nanotechnologies	CdTe/CdS	Canada	www.nntech.com
11	Ocean Nanotech	CdSe/ZnS, CdTe	AR	http://www.oceannanotech.com/
12	PlasmaChem	CdTe, ZnCdSe/ZnS	GER	www.plasmachem.de
13	Proteopure	-	PA	www.proteopure.com
14	QD Vision	-	MA	www.qdvision.com
15	SELAH Technologies	C based QDs	SC	www.selahtechologies.com
16	Sigma-Aldrich	CdS	MO	www.sigmaaldrich.com

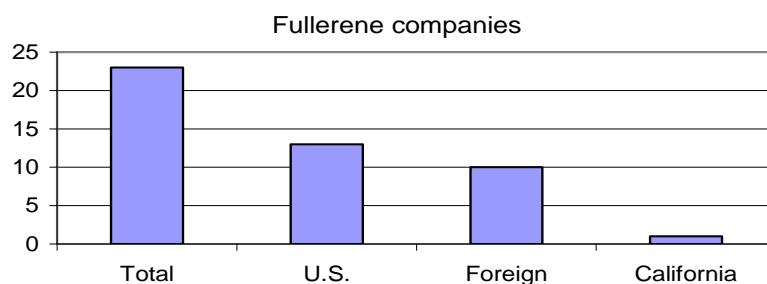
- -: information is not available
- Total: 16 companies
- US companies: 11, CA: 3/11
- Foreign companies: 5



3. Fullerenes companies list

	Name	Location	Web sites
1	Alfa Aesar	MA	www.alfa.com
2	American Dye source	Canada	www.adsdyes.com
3	BuckyUSA	TX	http://buckyusa.com
4	Cheaptubes	VT	http://www.cheaptubesinc.com/
5	Frontier carbon corp.	JPN	www.f-carbon.com
6	Honjo chemical	JPN	www.honjo-chem.co.jp
7	Ionic liquid technologies	GER	www.nanomaterials.iolitec.de/index_e.htm
8	JenLaur Ltd.	NC	www.janlaurtld.com
9	Luna Nanoworks	VA	www.lunananoworks.com
10	Materials technologies research	UK	www.mtr-ltd.com
11	MER corporation	AZ	www.opus1.com/~mercorp/index.htm
12	Mitsubishi Chemicals	JPN	http://www.mitsubishichemical.com/
13	MK nano	Canada	www.mknano.com
14	MTR	OH	www.mtr-ltd.com
15	Nano NB	Canada	www.nanonb.com
16	Nano-C	MA	www.nano-c.com
17	PlasmaChem	GER	www.plasmachem.com
18	SES research	TX	www.sesres.com
19	Smart engineering tools	MI	www.smttools.com
20	Strem Chemicals	MA	http://www.strem.com/code/index.ghc
21	TDA research	CO	www.tda.com
22	Term USA	CA	www.fullerenesforsale.com
23	Tokyo chemical industry	JPN	www.tci-asiapacific.com

- Total: 23 companies
- US companies: 13, CA: 1
- Foreign companies: 10



4. Metal oxides companies list

	Company name	Products	Location	Web sites
1	ABC Nanotech	SiO ₂	KOR	www.abcnanotech.com
2	Advanced Fibers & Powders	Al ₂ O ₃	PA	www.afpllc.net
3	Advanced Nano Products Co	ZnO, ITO, Ag, TiO ₂	KOR	www.anapro.com/english/default.asp
4	ALD nanosolution	SiO ₂ , Al ₂ O ₃	CO	www.aldnanosolution.com
5	Alpha Environmental	TiO ₂ , SiO ₂ , Al ₂ O ₃	CA	http://www.alpha-environmental.com/
6	AlphaNano technology	Fe ₂ O ₃ , SiO ₂	CHI	www.nanotubes.cn/index-en.htm
7	Altair nano	TiO ₂ , ZnO	NV	www.altairnano.com
8	AMAG Pharmaceuticals	Iron oxide	MA	www.amagpharma.com
9	American elements	SiO ₂ , ZnO, CeO ₂ , WO ₃	CA	www.americanelements.com
10	Antaria	ZnO, CeO ₂	Australia	www.antaria.com
11	Applied nanotech	ZnO	TX	www.appliednanotech.net
12	ARRY international	MgO, CeO ₂ , Al ₂ O ₃	Hong Kong	www.arry-nano.com
	Avanzare Innovacion tecnologica	ZnO, TiO ₂ , SiO, SiC, graphene	Spain	http://www.avanzare.es/
13	BASF	TiO ₂ , ZnO, CeO ₂	GER	www.basf.com/group/corporate/en/innovations/events-presentations/nanotechnology/index
	Buhler	TiO ₂ , ZnO, Fe-oxide	Swiss	www.buhlergroup.com
14	China rare metal material	CeO ₂ , Eu ₂ O ₃	CHI	www.china-raremetal.com
15	DA nanomaterials	SiO ₂ , Al ₂ O ₃	AZ	www.nanosurry.com
16	DuPont	TiO ₂	TX	www2.dupont.com/Titanium Technologies/en_US
17	Enviroclean	TiO ₂	FL	http://www.teamenviroclean.com/home
18	EVOnik	ZnO, CeO ₂ , ITO	GER	www.advancednanomaterials.com
19	Fuso chemical	SiO ₂	JPN	www.fusokk.co.jp/eng/index.html
20	Green millennium	TiO ₂	CA	www.greenmillenium.com
21	Green Nanolife	TiO ₂	CA	http://www.nanolifeusa.com/index.html
22	IBU Tec.	ZnO, Al ₂ O ₃ , SnO ₂	GER	www.ibu-tec.de
23	inframat	Cr ₂ O ₃ , ZrO ₂ , Al ₂ O ₃	NJ	www.inframat.com
24	Inframat Advanced Materials	Al ₂ O ₃ , TiO ₂ , CeO ₂	CT	www.advancedmaterials.us/index.htm
25	Ionic liquid technologies	Al ₂ O ₃ , SiO ₂	GER	www.nanomaterials.lolites.de/index_e.htm
26	Ishihara corp. USA	TiO ₂	CA	http://www20.inetba.com/ishiharacorpusa
27	Jiangsu Changtai Nanometer	TiO ₂	CHI	www.chinananometre.com.cn/eintro.htm
28	Keeling & Walker	SnO ₂	UK	www.keelingwalker.co.uk
29	Kemco International Asso.	Al ₂ O ₃ , CeO ₂ , ZnO	FL	http://www.kemcointernational.com/
30	Kon Corp.	TiO ₂	JPN	www.saga-kon.co.jp/english/product.html
31	Konarka	Solar cell film	MA	http://www.konarkatech.com/
	LEXON KOREA Corp.	SiO ₂ , TiO ₂	KOR	www.lexonkorea.com/eng-site/index.jsp
32	Mach I, Inc.	Fe ₂ O ₃	PA	www.machichemicals.com
33	Meliorum Technologies	CeO ₂ , Al ₂ O ₃ , ZnO	NY	http://www.meliorum.com/
34	MicroTechNano	Al ₂ O ₃	IN	http://www.microtechnano.com/
35	MK nano	Al ₂ O ₃ , ZnO, SiO ₂ , TiO ₂ , CeO ₂	Canada	www.mknano.com
36	MTI corporation	ZnO, CeO ₂ , TiO ₂	CA	http://www.mtixtl.com/
37	NanoAmor	TiO ₂ , Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃	TX	www.nanoamor.com
38	Nanocerox	CeO ₂	MI	http://www.nanocerox.com/
39	NanoChemonics	Iron oxide	VA	http://www.nanochemonics.com/
40	NanoCo	TiO ₂	KOR	www.nanoin.com
41	NanoE	Al ₂ O ₃ , ZrO ₂	FRA	www.nanoe.fr/index-vo.html
42	Nanogap	Fe ₂ O ₃	Spain	www.nanogap.es
43	NANOMAG	CeO ₂	KOR	www.nanomag.co.kr/eng
44	Nanomaterials	Al ₂ O ₃ , CaTiO ₃ , CeAlO ₃	PA	www.nanomaterialscompany.com
45	Nanomaterials Company	Al ₂ TiO ₅	PA	http://www.nanomaterialscompany.com/
46	Nanomaterials research unit	ZnO, MgO	Thailand	http://phycis.science.cmu.ac.th/nano
47	Nano-Oxides	TiO ₂ , CeO ₂ , Fe ₂ O ₃	UT	http://www.nano-oxides.com/
48	Nanophase Technologies	Al ₂ O ₃ , ZnO, CeO ₂ , Fe ₂ O ₃	IL	http://www.nanophase.com/
49	Nanopool	SiO ₂ spray coating	GER	www.nanopool.biz
51	NanoScale Corporation	CeO ₂ , ZnO, TiO ₂	KS	http://www.nanoactive.com/
53	Nano-size Ltd.	SnO ₂ , CuO	Israel	www.nano-size.com/index.htm
54	Nanux	TiO ₂	KOR	http://eng.nanocomposite.net
55	NEI corporation	CeO ₂ , MgO, MgAl ₂ O ₄	NJ	www.neicorporation.com
56	nGimat	CeO ₂ , Fe ₂ O ₃ , MgAl ₂ O ₄	GA	www.ngimat.com
57	NYACOL	CeO ₂ , Y ₂ O ₃ , ZnO ₂	MA	www.nyacol.com

58	Oxitian	TiO ₂	FL	www.oxitian.com
59	Oxonica	TiO ₂ , CeO ₂	CA	www.oxonica.com
60	PIDC	-	MI	http://www.pidc.com/
61	Pilkington	TiO ₂	CA	www.pilkington.com
62	PlasmaChem	Al ₂ O ₃ , TiO ₂ , CeO ₂	GER	www.plasmachem.de
63	Primet Precision Materials	TiO ₂	NY	http://www.primetprecision.com/
64	Qcells	Solar cell thin films	GER	http://www.qcells.de/en/solar_energy/index.html
65	Quantum sphere	Fe, Ag, Ni, Co, FeO, CuO	CA	http://www.qsinano.com/
66	Raymor nanotech	Al ₂ O ₃ , TiO ₂ , Cr ₂ O ₃	Canada	www.raymor-nanotech.com
67	Saint-Gobain	Al ₂ O ₃ , CeO ₂	CA	www.innovativeorganics.com
68	Sasol North America	Al ₂ O ₃ , Na ₂ O	LA	www.sasoltechdata.com
69	Seashell tech.	SiO ₂ , TiO ₂ , SnO ₂	CA	http://www.seashelltech.com/
70	Shanghai Allrun Nano	TiO ₂ , SiO ₂ , ZnO	CHI	www.allrunnano.com
71	Shanghai Huzheng NanoTech	TiO ₂ , SnO	CHI	www.hznano.com/en/index.asp
72	Showa Denko	TiO ₂ , ZnO	JPN	http://www.sdk.co.jp/html/english/index.html
73	Silco International	SiO ₂	OR	http://www.silco-intl.com/contact.html
74	Simax technologies	SiO ₂	CA	www.simaxtech.com
75	Stanford Materials (Impoter)	MgO, Al ₂ O ₃ , TiO ₂	CA	http://www.stanfordmaterials.com/
76	Sukgyung	SiO ₂ , MgO, ZrO ₂ , Y ₂ O ₃	KOR	www.sukgyung.com/index-en.htm
77	Sun nano	Y ₂ O ₃ :Eu, YVO ₄ :Eu, ZnO	CA	www.nanomaterialstore.com
78	Tayka Corporation	TiO ₂ , ZnO	JPN	http://www.tayca.co.jp/english/products/micro_titanium/use_01.html
79	TiPE	TiO ₂	CHI	www.tipe.com.cn/index.htm
80	Turbo bead	Fe ₂ O ₃	Swiss	www.turbobeads.com
81	TYR	Al ₂ O ₃	CHI	www.rareearthoxide.com
82	Umicore Nanomaterials	TiO ₂ , CeO ₂ , ZnO	Belgium	www.nanograin.umicore.com
83	Very small particle company	Metal oxide	Australia	www.vspc.com

- -: information is not available
- Total: 83 companies
- US companies: 45, CA: 13
- Foreign companies: 38

