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NANOSTRUCTURED MATERIALS AND MICRODEVICES FOR FOOD AND AGRICULTURAL APPLICATIONS

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Abstract

Nanostructured materials applications in food and agriculture are in an incipient stage but in the close future the need of tools and techniques developed by nanotechnology to detect and dissociate harmful substances and biosensors for improved and contamination free food and agricultural products will be increased. Some of these applications that have a potential for wider acceptance in the field of food and agricultural technologies will be approached in this paper.

***Keywords**: nanostructured materials, food/agricultural applications*

An overview on nanoworld

The word "nano" meaning "dwarf" in Greek language refers to dimensions on the order of magnitude of 10^{-9}. Nanotechnology deals with special properties of materials emerging from nanometer size, for example in biological systems, nanostructured organic and inorganic materials see fig.1. In the biological systems, the first level of organization occurs at the nanoscale structural level where all the fundamental properties and functions are systematically defined (Nalwa, 2000).

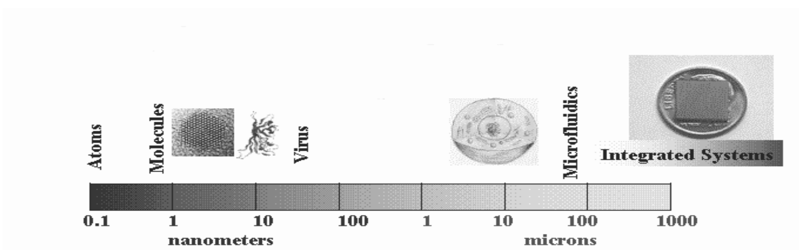

Fig. 1. Scale and the level of structure

Working at nano-level revolutionizes the scientific world by allowing scientists to manipulate matter at the atomic or molecular scale using physics, engineering, chemistry and biology (Roco, 1999). Nanotechnology is a broad and interdisciplinary area of research and development activity that has been growing fast, worldwide in the past years. It enables researchers to understand the relationship between macroscopic properties and molecular structure in biological materials of plants and animal origin (Kulzer, 2004) as well as atomic structure of materials in general. It is already having a significant commercial impact, which is increasing day by day. Using nanotechnology tools, scientists are able to self assemble atoms into structures with highly controlled properties e.g. nanowires (Huang, 2001; Hu, 1999), nanodots (Rueckes, 2000; Liu, 2003), self assembled molecules and particles (Duan, 2001), 3-D architecture (Vayssieres, 2001) etc. There are two basic forms of attaining nanomaterials "top-down" and "bottom-up". The term "atom" defines an object as the unbreakable, implying that it was possible to break down matter down to the level of individual atoms or molecules. This approach is termed as 'top-down' approach. This approach usually involves breaking of big chunks of materials (physically or chemically) into smaller objects of desired shapes and sizes. Complementary to "top-down" approach is the "bottom-up" approach or "self-assembly", which involves building up of macro-sized complex systems by combining simple atomic level components material. By this approach of arranging molecules one at a time, we can design complex systems by incorporating specific features which requires a good understanding of individual molecular structures and various molecular forces (Christoulakis, 2004).

Since the universe was created, to the first signs of life on this earth, self-organization has existed. Nature has developed many bioorganic molecules that form complex structures with very complex dynamic behavior, the living cells. These cells, self assemble and form further complex structures culminating in intelligent life forms like humans and other animals. Even when they are damaged, the living cells have an amazing ability to heal themselves by self-organization e.g. when a living cell is wounded, the body reacts by sending white blood cells to ward off the infections killing the germs, red blood cells and proteins form a seal cover over the wound and also nutrients to the cells, so that they can produce new cells to replace the damaged cells. Such biomaterials are usually made for specific applications inspiring the researchers to design materials that are ideal for specific application rather than to cut and trim natural materials to suit our needs. When the bottom-up process, one molecule at a time, builds materials it is possible to incorporate specific features at will. The concept of self-assembly with nanotechnology-changed radical the philosophical view in diverse fields ranging from biology to materials science (http://www.nano.gov/).

Nanotechnology will enable making high-quality products at a low cost and at a very fast rate. It is commonly referred to as a generic technology that offers better-built, safer, long lasting, cheap and smart products that will find wide applications in household, communications, medicine as well as food industry and agriculture amongst others. Currently the main thrust of research in nanotechnology focuses on applications like electronics, automation, medicine and life sciences (Blake, 1997). The experience gained from this can be used to modernize the food and agriculture systems. Novel agricultural and food quality control and monitoring systems, cellular biology, environmental protections, disease treatment drug delivery methods etc. are just a few examples where nanotechnology plays an important role.

Research in agriculture has always dealt with improving the efficiency of crop production, food processing, food safety and environmental consequences of food production, storage and distribution. Nanomaterials provide a new powerful tool to overcome these goals.

Applications

A. Nanosensors

Nanosensors can be defined than sensors at nanoscale. This means that it have the dimension in order of nanometers and can be used for determinations of different values in order of nanounits. The nanosensors are most usefully in biological and chemical analysis in which area the compounds are in this dimensional order (e.g. 6 carbon atoms means about 5nm, DNA diameter is in order of 5 angstroms, the red blood cell is approximate 20 microns diameter) (Nalwa, 2000). Many nanoscale sensor devices share commonalities with the device elements used for memory and logic IC’s in nanoelectronics, and thus suggests a natural interface between humans and digital computation/electronic systems. One of the nanosensors class is nanowire nanosensors. Interest in low-dimensional systems, such as zero-dimensional (0D) nanoclusters and one-dimensional (1D) nanowires, has been sparked by a desire to tune the fundamental optical and electronic properties of materials through rational control of their physical size (Hu, 1999). To realize the potential impact of these materials in nanoscale chemistry and physics, from both fundamental and applied viewpoints, demands materials of well-defined size, structure, and composition. One-dimensional materials, in contrast to 0D nanoclusters, have been relatively unexplored, primarily due to the synthetic challenge of producing high-quality materials of controlled size. The utility of nanowire materials in a myriad applications from devices and interconnects (Rueckes, 2000; Duan, 2001) for molecular computing to scanning probe microscopy tips emphasizes a definite need for high-quality nanowires (Wong, 1998). Because semiconductor nanowires can transport electrons and holes, they could function as building blocks for nanoscale electronics assembled without the need for complex and costly fabrication facilities. Boron- and phosphorous-doped silicon nanowires were used as building blocks to assemble three types of semiconductor nanodevices. Passive diode structures consisting of crossed *p*- and *n*-type nanowires exhibit rectifying transport similar to planar *p*-*n* junctions. Active bipolar transistors, consisting of heavily and lightly *n*-doped nanowires crossing a common *p*-type wire base, exhibit common base and emitter current gains as large as 0.94 and 16, respectively. In addition, *p*- and *n*-type nanowires have been used to assemble complementary inverter-like structures. The facile assembly of key electronic device elements from well-defined nanoscale building blocks may represent a step toward a "bottom-up" paradigm for electronics manufacturing (Cui, 2001a).

The monocrystal nanowires can serve as the basis for chemical and biological sensors in which detection can be monitored electrically (Bergveld, 1972). For example, a field effect transistor (FET) can be configured as a sensor by modifying the gate oxide (without gate electrode) with molecular receptors for the analyze of interest; binding of a charged species then results in depletion or accumulation of carriers within the transistor structure (Bergveld, 1972; Blackburn, 1987). An attractive feature of such chemically sensitive FETs is that binding can be monitored by a direct change in conductance fig. 2 where we see: (**A**) Schematic illustrating the conversion of a NW FET into NW nanosensors for pH sensing. The NW is contacted with two electrodes, a source (S) and drain (D), for measuring conductance. Zoom of the APTES-modified SiNW surface illustrating changes in the surface charge state with pH. (**B**) Real-time detection of the conductance for an APTES-modified SiNW for pHs from 2 to 9; the pH values are indicated on the conductance plot. (Inset, top) Plot of the time-dependent conductance of a SiNW FET as a function of the back-gate voltage. (Inset, bottom) Field-emission scanning electron microscopy image of a typical SiNW device. (**C**) Plot of the conductance versus pH; the red points (error bars equal ± 1 SD) are experimental data, and the dashed green line is linear fit through this data. (**D**) The conductance of unmodified SiNW (red) versus pH. The dashed green curve is a plot of the surface charge density for silica as a function of pH (Cui, 2001b). Fig. 3 shows real-time detection of protein binding. (**A**) Schematic illustrating a biotin-modified SiNW (left) and subsequent binding of streptavidin to the SiNW surface (right). The SiNW and streptavidin are drawn approximately to scale. (**B**) Plot of conductance versus time for a biotin-modified SiNW, where region 1 corresponds to buffer solution, region 2 corresponds to the addition of 250 nM streptavidin, and region 3 corresponds to pure buffer solution. (**C**) Conductance versus time for an unmodified SiNW; regions 1 and 2 are the same as in (B). (**D**) Conductance versus time for a biotin-modified SiNW, where region 1 corresponds to buffer solution and region 2 to the addition of a 250 nM streptavidin solution that was preincubated with 4 equivalents d-biotin. (**E**) Conductance versus time for a biotin-modified SiNW, where region 1 corresponds to buffer solution, region 2 corresponds to the addition of 25 pM streptavidin, and region 3 corresponds to pure buffer solution. Arrows mark the points when solutions were changed (Cui, 2001c).

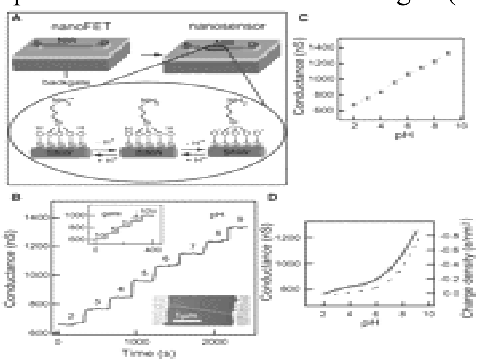

Fig. 2. NW nanosensor for pH detection (Cui, 2001b)

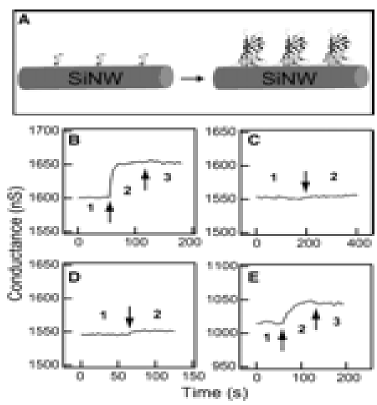

Fig. 3. Real-time detection of protein binding (Cui, 2001c)

B. Photocatalysis

Photocatalysis is one such application using nanoparticles, thin films and porous nanostructured materials (Christoulakis, 2004; Gagaoudakis, 2001; Gurlo, 1997; Hermann, 1999; Peral, 1997; Suchea, 2005). Photocatalysis is based on the double aptitude of the photocatalyst (essentially titania) to simultaneously adsorb both reactants and to absorb efficient photons. The basic fundamental principles are described as well as the influence of the main parameters governing the kinetics (mass of catalyst, wavelength, initial concentration, temperature and radiant flux). Besides the selective mild oxidation of organics performed in gas or liquid organic phase, UV-irradiated titania becomes a total oxidation catalyst once in water because of the photogeneration of OH^- radicals by neutralization of OH^- surface groups by positive photo-holes. A large variety of organics could be totally degraded and mineralized into CO_2 and harmless inorganic anions. Any attempt of improving titania's photoactivity by noble metal deposition or ion-doping was detrimental. In parallel, heavy toxic metal ions (Hg_2C, AgC, noble metals) can be removed from water by photodeposition on titania. Several water-detoxification photocatalytic devices have already been commercialized. Solar platforms are working with large-scale pilot photoreactors, in which are degraded pollutants with quantum yields comparable to those determined in the laboratory with artificial light (Hermann, 1999).

Photocatalysis is a reaction in which chemical compounds react in the presence of light and the compound is not completely consumed in the reaction (Hermann, 1999). Peral et al (1997) explained the use of photocatalysis for purification, decontamination and deodorization of air. Mills et al (1997) also explained semiconductor sensitized photosynthetic and photocatalytic processes for the removal of organics, destruction of cancer cells, bacteria and viruses.

Metal oxides like TiO_2 (Cao, 2002), ZnO (Christoulakis, 2004; Gagaoudakis, 2001; Suchea, 2005; Torres-Martinez, 1999), SnO_2 (Cao, 2002) etc. have been used for building photocatalytic systems. These nanoparticles as well as nanostructured thin films and porous materials have efficient bactericide rate due to another important property of nanoparticles in general, which is the increased surface to volume ratio (Fig. 4). The principle of photocatalysis could be used in the decomposition of toxic pesticides, which take a long time to degrade under normal conditions (Torres-Martinez, 1999).

The number of surface atoms increases when particle sizes decrease. This result in increased reactivity and other physical and chemical properties related to exposure to specific conditions, like photocatalysis, photoluminescence, etc (Dejneka, 2003; Nicewarner-Pena, 2001; Torres-Martinez, 1999).

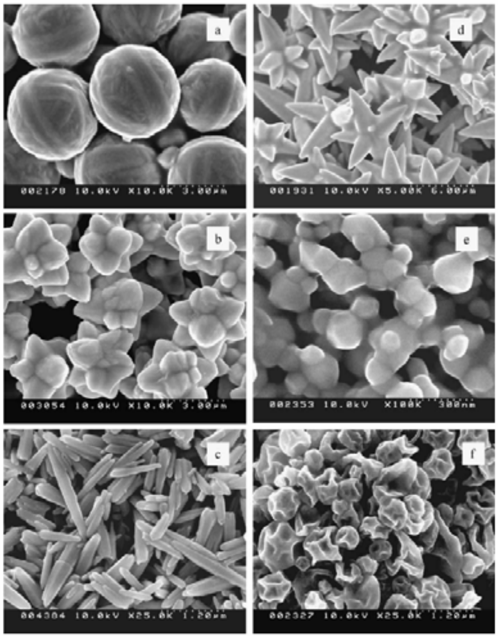

Fig. 4. SEM images of calcined ZnO powders (Li, 2003)

C. Identification tags

Identification tags are a part of our daily life today, right from application in wholesale agriculture and live stock products to consumer products. Ultra miniaturized identification tags have applications in the field ranging from advanced biotechnology to agricultural encoding. The possibility of large number of combinations of these nanobarcodes (> 1 million) makes them attractive also for use in multiplexed bioassays and general encoding. Dejneka (2003), describes micrometer sized glass barcodes doped with rare earth containing a specific type of pattern of different fluorescent materials that are identified by using UV lamp and optical microscope. Nanobarcode particles are encodeable, machine-readable, durable, submicron sized taggants as shown in (Fig. 5). They are freestanding, cylindrically shaped metal nanoparticles having dimensions of 20 -500 nm in diameter and 0.04 - 15 mm in length. The particles are manufactured in a semi-automated, highly scalable process by electroplating inert metals (gold, silver etc.) into templates defining particle diameter, and then releasing the resulting striped nano-rods from the templates (Fig. 6). Applications for these nanobarcodes are as ID tags for multiplexed analysis of gene expression and intracellular histopathology. The Nanobarcodes particles technology also holds great promise in non-biological applications, especially for robust, uniquely identifiable nanoscale tagging of small items for authentication or tracking in agricultural/food products. The technology will allow tagging of items previously not practical to tag with conventional barcodes, as well as aiding in the development of new Auto-ID technologies (http://www.nanoplextech.com/technology/nanobarcodes.htm).

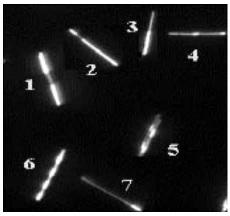

Fig. 5. Optical micrograph of a mixture of 7 flavors of Nanobarcodes (http://www.nanoplextech.com/technology/nanobarcodes.htm)

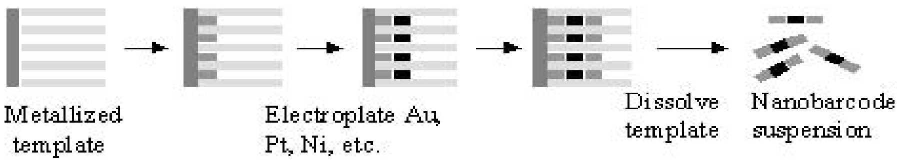

Fig. 6. Template-directed synthesis of Nanobarcodes particles (http://www.nanoplextech.com/technology/nanobarcodes.htm)

D. Contaminants detectors. Electronic noses

Bacteria are the most primitive life forms found almost in all places. We come into contact with millions of bacteria every day. They are in the air we breathe, in the food we eat and on the surfaces of most things we touch. Along with some useful bacteria there are numerous other disease causing bacteria. Recent advances in the field of luminescent nanocrystals have led to a new area of research in fluorescent labeling by quantum dots (QDs) with bio-recognition molecules. QDs have several prominent advantages over conventional organic fluorophores (dyes) as they are more efficient in luminescence compared to the organic dyes, their emission spectra are narrow, symmetric and tunable according to the particle sizes and material composition of the QDs and they show excellent photostability (Mills, 1997).

Due to their broad absorption spectra, they can be excited to all colors of the QDs by a single excitation light source. Su et al (2004) demonstrated a sensitive and rapid method for the detection of E. Coli O157:H7 using quantum dots (QDs) as a fluorescence marker coupled with immunomagnetic separation. They used magnetic beads coated with anti-E. coli O157 antibodies to selectively attach target bacteria, and biotin-conjugated anti-E.coli antibodies to form sandwich immuno complexes. After magnetic separation, the immuno complexes were labeled with QDs via biotin-streptavidin conjugation.

Microorganisms produce a range of characteristic volatile compounds that may be useful as well as harmful to human beings. e.g. Yeasts are beneficial for fermentation, bacteria eat sugar thereby producing alcohol as a by-product. Dairy products, bakery products and other food products are ideal media for rapid growth for a wide range of microorganisms. Bacteria are the most common cause of food rotting. The presence of foul odor is an indication for food rotting. Human nose can literally detect and distinguish thousands of odors, and this is sometimes impractical and could also be a further cause for poisoning. Applications include detecting contaminations in water supplies, raw food materials and food products as well as the processing lines – all of which require food producers to either hold on to inventory to complete the tests or simply release products which might be harmful. Enzymes can be used as a sensing element, since they are known to be very specific in attachment to certain biomolecules.

Electronic Nose (E-Nose) is a device mimicking the operation of the human nose, which uses a pattern of response across an array of gas sensors to identify different types of odors. The main purpose of the E-nose is to identify the odorant, estimate the concentration of the odorant and find characteristic properties of the odor as might be perceived by the human nose. The main components in an E-Nose are its gas sensors that identify odors. One such gas sensor functional diagram is shown in Fig. 7. These gas sensors are composed of nanoparticles, e.g. Zinc oxide nanowires whose resistance changes when a certain gas is made to pass over it (Alocilja, 2003; Christoulakis, 2004; Gagaoudakis, 2001). This change in resistance generates a change in electrical signal that forms the fingerprint for gas detection. This finger print pattern derived from the sensor is used to determine the type, quality and quantity of the odor being detected. The advantage of using nanoparticles is that they have improved surface area for better gas adsorption (fig. 2). Fig. 8 shows Scanning Electron microscope (SEM) and Atomic Force microscope (AFM) images of ZnO nanowires.

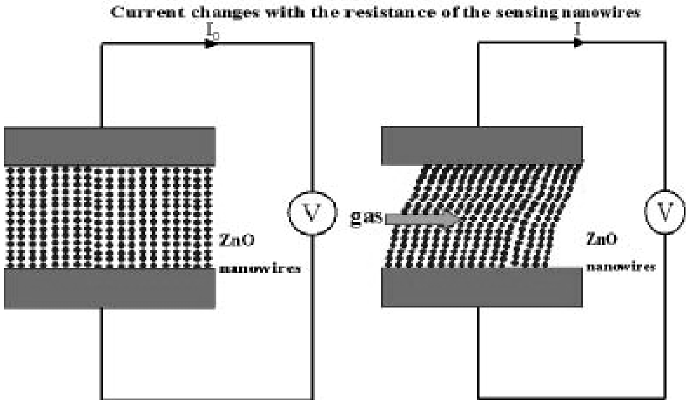

Fig. 7. Functional diagram of gas sensors whose current is a measure of change in resistivity of ZnO nanowires on gas adsorption (Chaniotakis, 2004)

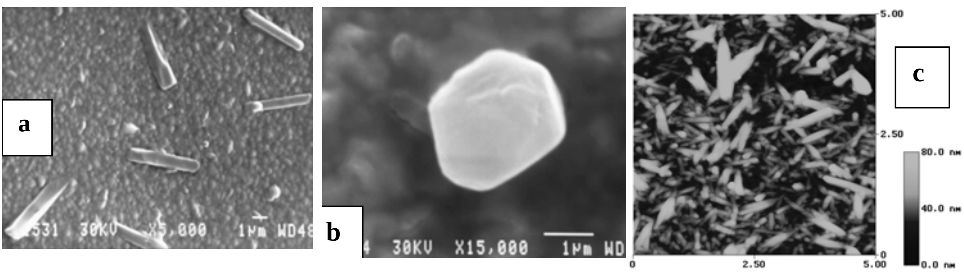

Fig. 8. Images of ZnO thin film surface growth from ceramic target by PLD technique: a), b) SEM, c) AFM. (Suchea, 2005)

Conclusions

Nanotechnology is now a part of our every day life. Research in nanotechnology has extremely high potential to benefit society through applications in agricultural and food systems. Any new technology carries an ethical responsibility for wise application and the recognition that there are potential unanticipated risks that may come with the tremendous positive potential. The first step is to inform the public about the advantages and challenges of nanotechnology. As public awareness increases, so will interest in the understanding of nanotechnology and new applications in all the domains will be found. Rapid testing technologies and biosensor related to the control of contamination of agricultural and food products are only some applications of nanotechnology. Food and agriculture technology should take advantage of the powerful tools of nanotechnology, for the benefit of humankind.

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