NANOSENSORS BASED ON METAL AND COMPOSITE NANOPARTICLES AND NANOMATERIALS

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Summary

Nanotechnology is the engineering and art of manipulating matter at the nanoscale. Nanoscaled inorganic composite materials have been used due to their high chemical inertness, non-swelling effect, high purity and rigidity. The versatility of physical and chemical properties of metal, semiconductor, noble and composite nanoparticles render them as promising materials in the fields ranging from optoelectronics to sensors. These nanoparticles or their self-assembles are able to discriminate the mixtures of gases,
volatile organic compounds, and odors. Advances in the fabrication of metal and noble metal nanoparticles have yielded nanostructured materials with distinctive properties, which can be potentially applied to (bio)sensors. The integration of metallic or semiconductive nanoparticles with organics and biomaterials (e.g., dyes, enzymes, nucleic acids, or antigens/antibodies) has led to the development of electrochemical or optical biosensors. Hybrid nanoscale materials are well established in various processes such as organic and inorganic compounds, nucleic acid detachment, protein separation, and immobilization of enzymes. Those nanostructures can be used as the building blocks for electronics and sensor devices because uniform metal coatings with the small and monodisperse domain sizes are crucial to optimize nanoparticle conductivity and to detect changes in conductivity and absorption induced by analyte adsorption on metal nanoparticle surfaces. The highly ordered assembly of zero-dimensional and one-dimensional nanoparticles is not only necessary for making functional devices, but also presents an opportunity to develop novel collective properties. Nanoscale semiconducting materials such as carbon nanotubes or nanowires show great potential for use as highly sensitive electronic sensors. In order to meet the specific requirements demanded by particular applications, the chemical modification of carbon nanotubes is essential. The derivatized carbon nanotubes differ from the crude material in their good solubility, which enables both a more extensive characterization and subsequent chemical reactivity. Quasi-one-dimensional semiconducting nanostructures, such as nanowires or nanobelts, are considered as an important multifunctional building block for fabricating various nanosensors and nanodevices. The field effect transistor is not only a basic electronic device but also exhibits a broad range of sensor applications. Semiconductor nanocrystals known as quantum dots have been increasingly utilized as biological imaging and labeling probes because of their unique optical properties, including broad absorption with narrow photoluminescence spectra, high quantum yield, low photobleaching, and resistance to chemical degradation. The surface modification of quantum dots with antibodies, aptamers, peptides, or small molecules that bind to antigens present on the target cells or tissues has resulted in the development of sensitive and specific targeted imaging and diagnostic modalities for in vitro and in vivo applications. Noble metal nanoparticles, with desirable nanoscaled sizes and unique physical properties - particularly the colors associated with their surface plasmon resonance- are highly suitable signal transducers for biosensors and building blocks in nanoassemblies. In particular, surface-enhanced Raman scattering nanosensors enable the chemical characterization of the nanometer vicinity of the gold nanoparticles and the measurement of vibrational spectra at a sensitivity and lateral resolution unachieved so far in other experiments. Micro- and nanofabricated cantilevers can provide a versatile platform for real-time, in situ measurements of physical, chemical, and biochemical properties of physiological fluids. New stimuli responsive properties were developed in N-isopropylacrylamide monomer and its derivatives around the critical temperature, above which its polymer precipitates out of solution or changes its volume, making it a valuable material for applications in sensing, analysis and microfluidics.

1. Introduction

In the last decade, the application of nanometer materials has received increasingly great attention in the field of nanotechnology, biotechnology and bioanalytical
chemistry. Nanotechnology is the engineering and art of manipulating matter at the nanoscale (1–100 nm). For environmental applications, nanotechnology offers the potential of novel functional materials, processes and devices with unique activity toward some contaminants, enhanced mobility in environmental media and desired application flexibility. Many nano-based environmental technologies (e.g., sensors, sorbents, and reactants) are under very active research and development, and are expected to emerge as the next generation environmental technologies to improve or replace various conventional environmental technologies in the near future.

Many fields of nanotechnology are based on physical and chemical interactions, involving nanoparticles of particular size and shape. Nanoparticles (NPs) played an important role in absorption/adsorption of (volatile) organic molecules and gases due to their large specific surface area and high surface energy. Nanoscaled inorganic materials have received much more attention because of their high chemical inertness, non-swelling effect, high purity and rigidity. In order to use the nanomaterials as sensors, one has to understand the peculiarities of both the synthesis and interaction mechanism during the sensing act. In recent years, the interest of researchers and engineers to gas- and liquid-sensitive materials has grown substantially due to the progress in nanotechnology. This interest is primarily connected to the promising electronic properties of nanomaterials, their size dependence, and the possibility of controlling the material structure by using new experimental techniques.

New generations of low power, low cost, and portable sensing devices are needed for monitoring of agriculture, chemistry, physics, medical, and manufacturing environments. With the recent developments in nanoscience and nanotechnology, there is a pressing need for flexible, mechanically robust, and environmentally stable chemical vapor sensors with a high efficiency and low power consumption. Among the main trends in the particle-gas-sensor nanotechnology, the creation of sensor arrays or “electronic noses” should be mentioned. Such multisensor systems can be fabricated on a single substrate, which can involve gas sensors of different types and, necessarily, the signal-processing systems. There are many examples of successive production of their nanostructured prototypes, which are able to discriminate the mixtures of gases, volatile organic compounds, and odors.

In recent years, tremendous attention has been paid to inorganic nanosize crystals because of their significant properties determined by the high surface areas and quantization of most electronic properties. Nanometer-sized inorganic particles potentially have unique properties because of quantum confinement effects and their large surface area relative to their volume. The versatility of physical and chemical properties of metal and semiconductor nanoparticles render them as promising materials in the fields ranging from optoelectronics, sensors to medicine. Thus far, great research interests have been involved in fabricating nanoparticle assemblies because they represent a popular route toward the preparation of advanced functional materials as well as a central concept in nanoscience and nanotechnology.

Recent advances in the fabrication of noble metal nanoparticles have yielded nanostructured materials with distinctive properties, which can be potentially applied to (bio)sensors, nonlinear optics, catalysis, telecommunications, and other fields. For
example, the functionalized gold particles have shown $10^4$ to over $10^7$ times signal enhancements on Raman spectroscopy (surface enhanced Raman scattering, SERS), more than 1000-fold enhancements on surface plasmon resonance (SPR) spectroscopy compared with nonparticle binding events, improvements of colorimetric sensing of DNA and other applications. These enhancements result from the particles’ collective properties, which are dependent on the particle’s dielectric function (optical properties of a single particle), the volume fraction of particles, and their spatial distribution. For metallic nanoparticles that are small compared to the wavelength $\lambda$ of an incident light, the dielectric function is known to be size-dependent, i.e., different from bulk values.

Significant challenges exist in assembling and interconnecting the building blocks of a nanoscale device and being able to electronically address or measure responses at the molecular level. Self-assembly is one of the few practical strategies or making ensembles of nanostructures and will therefore be an essential part of nanotechnology. In order to generate complex structures through self-assembly, it is essential to develop methods by which different components in solution can come together in an ordered fashion.

The preparation of novel magnetic nanocomposites or nanocrystals (NCs)/nanoparticles of improved properties are another important aspect in nanotechnology- and nanomaterials-related applications. Magnetically driven separations of small biological components and cells, detoxification of undesirable molecules and antigens, magnetic field-guided delivery of drugs and genes, relaxation and contrast enhancement in noninvasive magnetic resonance imaging (MRI) of tissues, piezoelectric immunosensors, and magnetic fluid hyperthermia for cancer therapy have been recently disclosed in those areas.

An advantage to applying biological recognitions to synthesize metal nanocrystals or nanoparticles is the efficient and reproducible nanocrystal production in the control of size and packing density without contaminating with precipitated metal aggregates. This is important when those nanoparticles are practically used as the building blocks for electronics and sensor devices because uniform metal coatings with the small and monodisperse domain sizes are crucial to optimize nanoparticle conductivity and to detect changes in conductivity and absorption induced by analyte adsorption on metal nanoparticle surfaces.

Within the general activities of nanotechnology, the use of biomaterial-nanoparticle hybrid systems for biosensor, bioelectronic, and circuitry applications has substantially advanced, and these efforts have established the rapidly developing field of nanobioelectronics and nanobiotechnology. For example, the integration of metallic nanoparticles with biomaterials (e.g. enzymes, nucleic acids, or antigens/antibodies) has led to the development of electrochemical or optical biosensors. Similarly, the integration of biomaterials with semiconductor nanoparticles has led to the development of optical or photovoltaic biosensor systems. Also, nanoparticles have been incorporated into biomaterials that act as templates, and the resulting structures have been grown into metallic or semiconductor nanocircuitry. This latter approach was suggested as a bottom-up miniaturization method for fabricating nanostructures with dimensions that are smaller than the presently achievable patterns using lithography.
The application of methodologies to produce nanoparticles with bioresponsive properties has opened the way for producing useful tools for molecular diagnostics, therapeutics, and biotechnology. Hybrid nanoscale materials are well established in various bioprocesses such as nucleic acid detachment, protein separation, and immobilization of enzymes. An important area of interest is the immobilization of proteins and enzymes on magnetic particles.

The reliance of future technologies on exploring facile and economic methods for the fabrication of one-dimensional (1D) systems has spurred intense and rapid development in the field of material synthesis. In particular, metal and semiconductor nanorods, as a family of 1D nanostructures, have been extensively pursued for their potential in building blocks for self-assembled nanoscale circuits, sensors and energy-conversion devices. The highly ordered assembly of such nanorods (NRs) is not only necessary for making functional devices, but also presents an opportunity to develop novel collective properties.

Nanoscale semiconducting materials such as carbon nanotubes (CNTs) or nanowires show great potential for use as highly sensitive electronic sensors. Single-walled carbon nanotubes (SWCNTs) arguably are the ultimate biosensor in this class for a number of reasons: SWCNTs have the smallest diameter (~1 nm), directly comparable to the size of single biomolecules and to the electrostatic screening length in physiological solutions. Covalent coupling of organic materials to CNTs is highly important. In order to meet the specific requirements demanded by particular applications (for example nanotube-based sensors or nanodevices), the chemical modification of CNTs is essential. Through the chemical functionalization of SWCNTs, the prerequisites for possible applications of such nanostructures have been established. The derivatized CNTs differ from the crude material in their good solubility, which enables both a more extensive characterization and subsequent chemical reactivity. Various defects in the carbon nanotube structure provide sites for their covalent derivatization.

Important chemical means to functionalize CNTs to yield systems of tailored solubility and structural features are desired. Nonetheless, the integration of CNTs with other electronic materials, such as conductive polymers or nanoparticles, is anticipated to generate materials of new properties and functions. The use of biomolecules as templates for fabricating metal contacts may be a major advance. With these advances in the area of the organic or biomolecule-CNT hybrid systems, one may look forward to exciting new applications.

Nanowire-based field-effect transistors (FET) have been widely used for detection of a variety of biological and chemical species, detection of pH value, detection of metal ions, viruses, proteins, etc. In most of these applications, the mechanism of sensing is based on the functionalization of a homogeneous semiconducting nanowire, such as silicon and In2O3 nanowires. The extreme sensitivity of nanowire (NW) and nanotube (NT) field-effect sensors originates from their one-dimensional structure that enables efficient charge transfer between the surface-anchored biomolecules and NW/NT. However, they are also highly sensitive to impurities and other ionic species in analyte solution, especially at the acclaimed low DNA concentration.
Quasi-one-dimensional semiconducting nanostructures, such as nanowires (NWs) and nanobelts (NBs), are considered as an important multifunctional building block for fabricating various nanodevices. Owing to their unique electronic, optical, and piezoelectric properties, for example, ZnO NWs/NBs have been successfully applied in field effect transistors, sensors, and piezoelectric devices. The field effect transistor is one of the most studied systems since it not only is a basic electronic device but also exhibits a broad range of sensor applications. The mechanism of nanowire sensors for sensing gases, biomolecules, or even virus relies on the creation of a charge depletion zone in the semiconductor nanowire by the surface adsorbed sensing targets.

Semiconductor nanocrystals known as quantum dots (QDs) have been increasingly utilized as biological imaging and labeling probes because of their unique optical properties, including broad absorption with narrow photoluminescence spectra, high quantum yield, low photobleaching, and resistance to chemical degradation. In some cases, these unique properties have conferred advantages over traditional fluorophores such as organic dyes. The surface modification of quantum dots with antibodies, aptamers, peptides, or small molecules that bind to antigens present on the target cells or tissues has resulted in the development of sensitive and specific targeted imaging and diagnostic modalities for in vitro and in vivo applications. Quantum dots, fluorescent colloidal semiconductor nanoparticles, have been developed to provide materials compatible in size with biomolecules for use as fluorescent biosensors as they are reasonably resistant to photobleaching, to denaturants of biomolecules, and to alterations in pH and temperature.

Gold nanoparticles, with desirable nanoscaled sizes and unique physical properties (particularly the colors associated with their surface plasmon resonance (SPR)), are highly suitable as signal transducers for biosensors and building blocks in nanoassemblies. In particular, surface enhanced Raman scattering (SERS) nanosensors enable the chemical characterization of the nanometer vicinity of the gold nanoparticles and the measurement of vibrational spectra at a sensitivity and lateral resolution unachieved so far in other experiments. There is compelling evidence that high SERS enhancement levels are associated mainly with enhanced local optical fields. This implies that the SERS enhancement factor depends strongly on the morphology (e.g., the size, shape, or aggregation) of the nanoparticles. Composite nanoparticles with gold nanoshells are fascinating nanoparticles composed of a spherical dielectric core coated with a nanometer thin gold layer. Their scattering spectra show a pronounced resonance in the visible range, similar to solid noble-metal nanospheres. The origin of this resonance behavior is a collective oscillation of the conduction band electrons, which is known as the nanoparticle plasmon (NPP).

The polymerization of N-isopropylacrylamide (NIPAM) have been explored because poly(NIPAM) (PNIPAM) is well-known for its characteristic lower critical solution temperature (LCST) in water at 32 °C, above which it precipitates out of solution, makes it a valuable material for applications in bioanalysis and microfluidics. The same property was of interest to us also to quickly assess whether polymer chains were formed by raising the temperature above the LCST. New stimuli responsive properties of PNIPAM are based on the precipitation of polymer out of solution or changes to its
volume, making it a valuable material for applications in sensing, analysis and microfluidics.

In some specific applications, it would be highly desirable to modulate the spatial distribution between nanoparticles arising from the change in polymer chain conformations in response to some external chemical or biochemical species. For example, the nanosensors based on the CdSe nanoparticles immobilized on pH-responsive poly(2-vinyl pyridine) (P2VP) brushes were studied. It has been realized that stimuli-responsive variation in the thickness of polymer brushes leads to the change in optical properties of immobilized nanoparticles and hence opens the new avenue for fabrication of nanosensors. Owing to the multifunctional properties of silver nanoparticle and responsiveness of P2VP brushes with the pH of surrounding media, the obtained P2VP-silver nanoassemblies can be used as pH nanosensors.

Conjugated polymers are emerging materials for biological sensor applications because of their signal amplification property and environmental sensitivity. Moreover, controlled assembly of fluorescent sensory polymers expands the dimensionality of the energy transport properties from one-dimensional (1D) to two-dimensional (2D) and to three-dimensional (3D) efficiently, augmenting the intrinsic high sensitivity even further. For example, conjugated polymers based on phenyleneethynylene, polyacetylene, orinorganicpolymetalloles are efficient optical sensors for nitroaromatics.

Design and fabrication of chemical sensors has become one of the most active research fields due to their diverse practical and potential applications. To improve the sensing characteristics, a general route is to make chemical sensors at the nanoscale, taking advantage of the large surface areas of nanoscale structures. Chemical nanosensors based on one dimensional carbon, silicon, and ceramic nanostructures are of particular interest because of their high surface to volume ratio and special physical and chemical properties. A chemical sensor based on the simple change in resistance in response to the binding of analytes. Advantages of chemiresistors include low power consumption and the ease of high precision resistance measurements. Several materials have been utilized as gas sensors, including metal oxides, organic semiconductors, and carbon nanotubes. Metal oxides are the most widely used materials for chemiresistors. Despite their sensitivity, the applications of these materials have been limited by high power consumption and poor selectivity. Organic semiconductors, especially conjugated polymers, have long been considered as chemiresistor materials. The integration of molecular recognition into their structures is attractive; however, these materials are limited by electrostatic/dielectric interferences and fragile organic metal interfaces. Among the chemical nanosensors, the humidity nanosensor is very important for their practical applications in environment monitoring, industrial process control, and our daily life. Many humidity nanosensors based on 1D nanostructure have been successfully obtained. However, the sensing characteristics (e.g., response, recovery, reproducibility, stability, and linearity) still need to be improved.

Electrochemical sensors provide unlimited opportunities for monitoring environments and making the world safer and cleaner. Such devices meet the environmental and security demands for monitoring electroactive pollutants or threat agents with high
sensitivity, selectivity, and temporal resolution. Electrochemical detection is of particular significance in the development of aptasensors since it allows for high sensitivity and selectivity, simple instrumentation, as well as low endogenous background. Many electrochemical strategies only incorporate the aptamer-target binding events into the sensor design, and the presence of target is signaled either via direct measurements of electrochemical parameters such as impedance and potential or through indirect detection of certain exogenous labels including enzymes and nanoparticles. Another conceptually distinct mechanism for electrochemical aptasensors is based on conformational changes induced by strand displacement or structure switching.

Microcantilevers are nanomechanical transducers, which convert intermolecular reaction forces to detectable cantilever deflection in nanometers. When specific reactions among (bio)molecules occur on one surface of a cantilever, the reactions induce a change in the surface stress as a result of the free energy reduction. The cantilever deflects due to the change of surface stress and indicates the occurrence of the specific chemical and biomolecular reaction. To achieve sensitive and repeatable performance of microcantilever sensors for the detection of intermolecule interactions, one can explore different surface chemistries for passivation of inactive surfaces and several different surface chemistries for functionalization of active surfaces with probe molecules (antibodies).

The terms “actuator”, “sensor”, and “transducer” are used in the description of measurement systems—sometimes interchangeably. In the broadest sense, a transducer receives energy from one system and transmits this energy to another system, often in a different form. A sensor monitors a system; it responds to physical stimuli, such as heat, light, pressure, or motion, and generates an electronic impulse for detection. An actuator, on the other hand, imposes a state upon a system. Most commonly, this involves converting an input electrical impulse into motion. Thus, actuators and sensors are both transducers intended for different tasks. In accord with these general definitions, an electromechanical transducer converts electrical energy into mechanical energy, and vice versa.

In this chapter, we focus on summarization and discussion of literature data on the most central concern in sensor and nanotechnology: preparation, properties and functioning of sensor at the nanoscale range shortly above mentioned.

2. Metal Nanoparticle Sensors

Nanoparticles are nanometer-size materials with unique physical and chemical properties and have been widely used for many years. Organic molecules, also in the nanometer-size range, possess functionalities that enable recognition and self-assembly. The combination of nanoparticles and chemical or biological molecules is very attractive and has gained tremendous attention from academics and industry, because such a combination could create new materials for electronics and optics and lead to new applications in genomics, proteomics, and biomedical and bioanalytical areas. For environmental applications, nanometer-size particles and their self-assemblies offer the potential of novel functional materials, processes and devices with unique recognition
activities, enhanced mobility in environmental media and desired application flexibility. Many nano-based environmental technologies (e.g., sensors,..) are under very active research and development, and are expected to emerge as the next generation environmental technologies to improve or replace various conventional environmental technologies in the near future.

The preparation of nanomaterials is one of the most active fields in material science. A number of techniques have been used for the production of nanoparticles: gas-evaporation, sputtering, sol-gel method, hydrothermal, microemulsion, polyols, laser pyrolysis, sonochemical synthesis, chemical coprecipitation, and so on. Among them, the surfactant assembly mediated synthesis is attracting more attention because it allows for a good control of the synthesis process at ambient reaction condition. Experimental parameters such as pH, reactant concentrations, stirring speed, titration rate, reaction time and external temperature can, to some extent, influence the composition and surface properties of produced metal nanoparticles and hence need to be maintained constant in the experiments to produce consistent samples. Other methods based on a modified sol–gel technique as well as on the original approach that uses the mechanochemical milling, were also employed for improving the sensor performance of nanostructured metal and metal-oxide materials. Besides enhancing the characteristics of existing gas- and liquid- sensitive elements, nanotechnology also promotes the development of new types of composite nanomaterials for microelectronics and sensors.

New prospects in designing nanosensors based on nanoparticles were opened by the synthesis of new metal and noble metal nanoparticles. It was shown that pore-free crystals of some nanocrystals can reversibly take up and evolve gas without breaking the crystal, that is, the nanocrystals can breathe. For example, when interacting with gas (sulfur dioxide, chlorine, carbon dioxide,..), a crystal changes the color. The change in its color can be attributed to the transition of square-planar complexes of nanoparticles into square pyramidal complexes of nanoparticles with liquid or gas, for instance, as the fifth ligand. In doing so, the crystal increases in volume, while retaining the ordered lattice structure. Yet a more interesting result is obtained if a crystal with increased volume is exposed to air. In this case, the crystal “breathes out” gas and relaxes to its original, colorless, and gas-free state. This process can be repeated many times without breaking the crystal.

In comparison with polymer matrices and biomembrane-like films inorganic materials are thermally stable and chemically inert in aqueous and nonaqueous solutions. Many inorganic materials, such as clays, sol–gels, nanoparticles and carbon nanotubes have been proven to be the promising matrices to construct (bio)sensors. Mesoporous materials have attracted attention these years in protein immobilization because of their unidirectional pore topologies and large surface areas. However, the pore of mesoporous materials is rigid, so the uptake of guest species is limited by the minimal channel cross-section.
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Kulys J., Wang L. and Maksimoviene A. (1993). L-lactate oxidase electrode. based on methylene green and carbon paste. *Analytica Chimica Acta* **274**, 53–58. [This paper describes the rapid and accurate determination of hydrogen peroxide which is of great importance because it is not only the product of the reactions catalyzed by many highly selective oxidases but also an essential compound in food, pharmaceutical and environmental analyses].


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dependence of the nanoparticle plasmon resonance position on the refractive index of the particles’
surroundings).

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sorbents, and reactants) which are under very active research and development, and are expected to
emerge as the next generation environmental technologies to improve or replace various conventional
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the microcantilever sensor functionalized with a Ge–S–AgI coating upon exposure to water, ethanol,
acetone, and ammonia vapours with different concentrations in a gas-flow mode]

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information on magnetically driven separations of small biological components and cells, detoxification
of undesirable molecules and antigens, magnetic field-guided delivery of drugs and genes, relaxation and
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immunosensors, and magnetic fluid hyperthermia for cancer therapy]

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sensitive to subtle differences in preparation and purification of proteins that are otherwise identical and
cannot be differentiated using other techniques]

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cantilever biosensor for differentiation of low density lipoproteins (LDL) and their oxidized form
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self-signal amplifying DNA microarrays bioconjugated to the PPE film to form a conjugated polymer-based signal amplifying sensor film.


Raiteri R., Nelles G., Butt H.-J., Knoll W. and Skladal R. (1999). Sensing of biological substances based on the bending of microfabricated cantilevers. Sensors and Actuators B 61, 213-217. [This is a study reporting on surface stresses leading to mechanical bending of cantilevers].

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with detectors of surface stresses at extremely small mechanical forces.


Shih W.M., Quispe J.D. and Joyce G.F. (2004). A 1.7-kilobase singles-strand DNA that folds into a nanoscale octahedron. *Nature* 427, 618-621. [This is a study on how one may utilize biomolecules, to grow nanoparticles, and to employ the optical properties of the synthesized nanoparticles to follow the biocatalytic processes].


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potentials with arrays of AlGaN/GaN electrolyte-gate field effect transistors.


Talley C.E., Jusinski L., Hollars C.W., Lane S.M. and Huser T. (2004). Intracellular pH sensors based on surface-enhanced raman scattering. Analytical Chemistry 76, 7064-7068. [This investigation demonstrated the use of SERS in cells, using gold or silver nanoparticles and reporter molecules and the SERS spectra of selected reporter molecules were shown to depend on the pH value in the environment of the metal nanostructures].


Tan C., Atas E., Müller J.G., Pinto M.R., Kleiman V.D. and Schanze K.S. (2004). Amplified quenching of a conjugated polyelectrolyte by cyanine dyes. Journal of the American Chemical Society 126, 13685. [This study discusses the controlled assembly of fluorescent sensory polymers which expands the dimensionality of the energy transport properties from 1D to 2D and to 3D efficiently].

Tang X., Bansaruntip S., Nakayama N., Yenilmez E., Chang Y. and Wang Q. (2006). Carbon Nanotube DNA Sensor and Sensing Mechanism. Nano Letters 6, 1632-1636. [This contribution is devoted to development of electronic DNA sensors based on carbon nanotube field effect devices, which are readily scalable to high density sensor arrays and amenable to integration with “lab-on-a-chip” microanalysis systems].

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Tokareva I., Minko S., Fendler J.H. and Hutter E. (2004). Nanosensors Based on Responsive Polymer Brushes and Gold Nanoparticle Enhanced Transmission Surface Plasmon Resonance Spectroscopy. Journal of the American Chemical Society 126, 15950-15951. [335] [This is a case study reporting on the
nanosensor of gold nanoparticle/polymer conjugates showing enhanced transmission surface plasmon resonance (T-SPR) spectroscopy.

Tsai Y.C., Li S.C. and Liao S.W. (2006). Electrodeposition of polypyrrole–multiwalled carbon nanotube–glucose oxidase nanobiocomposite film for the detection of glucose. *Biosensors and Bioelectronics* **22**, 495–500. [This study indicates that carbon nanotubes are attractive materials for application to biosensors due to the low-potential detection of hydrogen peroxide and β-nicotinamide adenine dinucleotide (NADH) and the minimal surface passivation during the electrochemical oxidation of NADH].

Uemura T., Ohba M. and Kitagawa S. (2004). Size and Surface Effects of Prussian Blue Nanoparticles Protected by Organic Polymers. *Journal of Inorganic Chemistry* **43**, 7339–7345. [In this work tremendous attention has been paid to inorganic nanosize crystals because of their significant properties determined by the high surface areas and quantization of most electronic properties].


Valério C., Alonso E., Ruiz J., Blais J.-C. and Astruc D. (1999). A polycationic metalloendrimer with 24 \([Fe(η^5-C5Me5)(η^6-N-alkylaniline)]^+\) termini that recognizes chloride and bromide anions. *Angewandte Chemie International Edition* **38**, 1747-51. [This document reports on the recognition of \(H_2PO_4^-\), \(HSO_4^-\), and \(Cl^-\) and \(Br^-\) by metalloendrimers].


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Wang D.Y., Lai B.H.Y. and Sen D. (2002). A General Strategy for Effector-mediated Control of RNA-cleaving Ribozymes and DNA Enzymes. Journal of Molecular Biology 318, 33-43. [This reports on increased range of analytes that can be detected by using enzymes to analytes such as adenosine by introducing aptamers into the above DNAzyme system to form aptazymes].


Wang J. (2005). Nanomaterial-Based Amplified Transduction of Biomolecular Interactions. Small 1, 1036-43. [This study opens the application of methodologies to produce nanoparticles with bioresponsive properties for producing useful tools for molecular diagnostics, therapeutics, and biotechnology].


Wang J. and Musameh M. (2003). Carbon Nanotube/Teflon Composite Electrochemical Sensors and Biosensors. Analytical Chemistry 75, 2075-2079. [This study reports on the electrocatalytic oxidation of NAD(P)H [NAD(P)H = 1,4-dihydronicotinamide adenine dinucleotide (phosphate)] cofactors and the reduction/oxidation of hydrogen peroxide stimulated by CNTs based biosensors].

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Wang J., Musameh M. and Lin Y. (2003). Solubilization of Carbon Nanotubes by Nafion toward the Preparation of Amperometric Biosensors. Journal of the American Chemical Society 125, 2408–2409. [This contribution reports on the ability of CNTs to promote the electron-transfer reactions of NADH and H₂O₂ for dehydrogenase- and oxidase-based amperometric sensor].

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**Bibliography Sketch**

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