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Aims and Scope

Chemical sensors and biosensors are becoming more and more indispensable tools in life science, medicine, chemistry and biotechnology. The series covers exciting sensor-related aspects of chemistry, biochemistry, thin film and interface techniques, physics, including opto-electronics, measurement sciences and signal processing. The single volumes of the series focus on selected topics and will be edited by selected volume editors. The *Springer Series on Chemical Sensors and Biosensors* aims to publish state-of-the-art articles that can serve as invaluable tools for both practitioners and researchers active in this highly interdisciplinary field. The carefully edited collection of papers in each volume will give continuous inspiration for new research and will point to existing new trends and brand new applications.

Preface

Nanomaterial is one of the hottest fields in nanotechnology that studies fabrication, characterization, and analysis of materials with morphological features on the nanoscale in at least one dimension. Recent progress in synthesis and fundamental understanding of properties of nanomaterial has led to significant advancement of nanomaterial-based gas/chemical/biological sensors. The most important aspect of nanomaterial is their special properties associated with nanoscale geometries. The most fundamental characteristic of nanomaterial is the high surface area to volume ratio, which results in a number of unusual physical and chemical properties such as high molecular adsorption, large surface tension force, enhanced chemical and biological activities, large catalytic effects, and extreme mechanical strength, but another unique property of nanomaterial and recently most studied is the quantum size effect that leads to their discrete electronic band structure like those of molecules. This quantum property of nanomaterial can lead to an extraordinary high sensitivity and selectivity of biosensors and can be benefit to the field of diagnostics.

In this book, we focus on a wide range of nanomaterials including nanoparticles, quantum dots, carbon nanotubes, molecularly imprinted nanostructures or plastibodies, nanometal, DNA-based structures, smart nanomaterials, nanoprobes, magnetic nanomaterials, organic molecules such as phthalocyanines and porphyrins, and the most amazing novel nanomaterial called graphene, for various gas/chemical/biological sensing applications. Moreover, perspectives of new sensing techniques such as nanoscaled electrochemical detection, functional nanomaterial-amplified optical assay, colorimetric fluorescence, and electrochemiluminescence are reviewed and extensively explained. This book includes recent progress of selected nanomaterials over a broad range of gas/chemical/biological sensing applications, and examples of nanomaterials in sensing and diagnostic application are given.

The use of biofunctional nanomaterials in signal amplification for ultrasensitive biosensing is extensively discussed. The biofunctional nanomaterials with the abilities of specific recognition and signal triggering can be employed as not only excellent carriers but also electronic and optical signal tags to amplify the detection signal. Nanomaterial-based electroanalytical biosensors are discussed to give some ideas and concepts of utilizing nanomaterials for cancer and bone disease diagnostics. Then, new nanomaterial-based electrochemical impedance biosensors applied in cancer and bone disease studies that can detect in real time without any pre-labeling specific biomolecules at previously unattainable ultra-low concentrations are specifically discussed. The hottest area of nanomaterial called "carbon nanomaterial" including carbon nanotube and graphene is up-to-date reviewed. Carbon nanotube-based chemical and biosensors and its integration to microfluidic systems are discussed. Carbon nanotube-based electrochemical sensors integrated into microfluidic systems are extensively surveyed and discussed. Moreover, a comprehensive review of graphene-based chemical and biosensors will help who interests to springboard to the new area of carbon nanomaterial-based sensors more easily. Graphene's synthesis methods, properties, and different types of chemical and biosensors including chemoresistive, electrochemical, and other sensing platforms are described. Newly invented organic nanomaterials such as molecularly imprinted polymers (MIPs) are expansively reviewed and analyzed for sensing and diagnostics of various biological species. Inorganic nanomaterials such as nanometal structures using in localized surface plasmon resonance (LSPR) biosensor platform are discussed including their biomedical diagnosis applications. Naturally derived nanomaterial-based sensors such as DNA sensors (genosensors) employing nanomaterials are extensively described. As quantum effect of nanomaterial is amazing, novel nanoprobes for in vivo cell tracking used for evaluating the therapeutic efficacy will show the potential of this quantum effect for diagnostics. Another organic nanomaterials made of metallo-porphyrin (MP) and metallo-phthalocyanine (MPc) which are optically active are used in optical-based gas sensors and electronic nose systems. Then, this book concludes with the uses of nanotechnology to attain highly sensitive detection in electrochemical microdevices. Issues relating to miniaturization of electrochemical electrode and system are discussed. Various techniques applicable to fabrication and integration of nanoelectrodes are included. With the extensive review of newly discovered nanomaterials used for sensors and diagnostics, this book will be interesting not only for scientists working in the field of nanomaterial-based sensor technology but also for students studying analytical chemistry, biochemistry, electrochemistry, material science, and micro- and nanotechnology.

Pathumthani, Thailand Adisorn Tuantranont

Contents

Nanomaterials for Sensing Applications: Introduction and Perspective

Adisorn Tuantranont

Abstract Recent progress in synthesis and fundamental understanding of properties of nanomaterials has led to significant advancement of nanomaterial-based gas/chemical/biological sensors. This book includes a wide range of nanomaterials including nanoparticles, quantum dots, carbon nanotubes, graphene, molecularly imprinted nanostructures, nanometal structures, DNA-based structures, smart nanomaterials, nanoprobes, magnetic-based nanomaterials, phthalocyanines, and porphyrins organic molecules for various gas/chemical/biological sensing applications. Perspectives of new sensing techniques such as nanoscaled electrochemical detection, functional nanomaterial-amplified optical assay, colorimetric, fluorescence, and electrochemiluminescense are explored.

Keywords Chemical and Biosensors, Gas, Nanomaterials

Contents

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1 Introduction to Nanomaterials and Their Sensing Applications

Nanomaterial is one of the major fields in nanotechnology that studies fabrication, characterization, and analysis of materials with morphological features on the nanoscale in at least one dimension [1–5]. The nanoscale is usually defined as the size that is smaller than 100 nm. However, it is sometimes extended to a dimension smaller than 1 μm. Recently, the European Commission adopted the definition of a nanomaterial as a natural, incidental, or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm. In specific cases, the number size distribution threshold of 50% may be replaced by a threshold between 1% and 50%.

Nanomaterials may be classified based on dimensionality (D) of their features into 0D, 1D, 2D, and 3D nanostructures [6]. 0D nanostructures including nanoparticles, nanospheres, quantum dots, isolated molecules and atoms are point structures with nanoscale in all dimensions [7–9]. 1D nanostructures including nanotubes and nanowires are structures with non-nanoscale only in one dimension [8, 10–12]. 2D nanostructures such as nanosheet, nanoplates, nanobelts, and nanodisc are structures with nanoscale in one dimension [13–16]. Lastly, 3D nanostructures such as nanotetrapods, nanoflowers, and nanocombs are arbitrary structures, which contain nanoscale features in any of three dimensions [17, 18]. These nanomaterials can be made of large variety of functional materials, including metals, metal oxides, ionic compound, ceramics, semiconductors, insulators, organics, polymers, biological materials, bioorganisms, and so on. Each functional material can be made in many nanostructure forms. Carbon is one of the most notable examples that all dimensionalities of 0D fullerene (hollow bucky ball) [19], 1D carbon nanotubes (CNTs) [20–23], 2D graphene [13], and 3D graphite nanostructures are available. Apart from carbon, a wide range of nanomaterials with different dimensions of metal [24, 25], metal oxide [8, 15, 26–28], semiconductor [29–33], organic [11, 34, 35], polymers [36], biomaterials [37–40], and their composites [39, 41–44] have been widely reported.

Various forms of nanostructured materials can be synthesized or fabricated by many different methods. In general, nanomaterials can be made by three main approaches, including top-down, bottom-up, and the combination [45–47]. In the first approach, bulk starting materials will be broken down into nanoscale structures by various methods such as photolithographic patterning, wet etching, plasma etching, reactive-ion etching, laser processing, electrochemical etching, and grinding [30, 48–51]. The approach can be used for production of nanoparticles, nanorod, and nanowires of metal oxide, semiconductor, metal, and polymer materials. The main advantages of these methods include well-controlled parameters and large-scale manufacturability. However, they suffer from high material loss, relatively high cost, and slow production rate.

For the second scheme, nanostructures are formed by assembly of atoms or molecules controlled by suitable process parameters of each process [52]. Bottom-up methods are more widely used because they can be better controlled, faster, and more cost effective [53]. Bottom-up schemes can be mainly divided into vapor-phase and solution-route syntheses, in which nanostructures are built up from molecules or atoms in gas and liquid phases, respectively. Widely used vapor-phase methods include chemical vapor deposition (CVD) [54, 55], plasma-enhanced CVD [56, 57], atomic layer deposition [58, 59], thermal/e-beam evaporation [60–62], pulse laser deposition [63–65], sputtering [66], and flame-based synthesis [67]. These techniques have been widely applied for syntheses of metal oxide, semiconductor, metal, and composite nanostructures such as nanoparticles, nanowires, nanotetrapods, nanorods, nanobelts, nanosheets, and nanotubes made of carbon, SnO_2, TiO_2, ZnO, Si, GaAs, Ti, W, etc. They offer several advantages including well-controlled parameters, high-quality and aligned structure, very low contamination, and large-scale manufacturability. However, they normally involve expensive instrumentation, vacuum system, and high-temperature process.

Solution-phase methods including precipitation [68], sol–gel deposition [69], hydrothermal/solvothermal syntheses [70–72], electrochemical deposition [73], self-assembled monolayer [16], molecular self-assembly [74, 75], electrospinning [76, 77], electrospray [78], spray pyrolysis [79], and other chemical routes [80] are relatively simple, of low temperature, and of low cost. They are more suitable for syntheses of organic, polymer, and biological nanomaterials such as nanofibers, nanoparticles, nanosheets of phthalocyanines, porphyrins, polyanilene (PANI), poly (3,4 ethylenedioxythiophene):poly-styrene-sulfonic acid (PEDOT:PSS), polypyrol, polyvinlypyrolidone (PVP), polyacrylonitride (PAN), oxidase enzymes, and deoxyribonucleic acid (DNA) [81–89]. Nevertheless, these methods can also be used to synthesize some metal oxide, semiconductor, metal nanostructures such as nanowires of Au, Ni, Fe, and TiO_2, which often rely on self-assembly of polymer and biological materials such as cells and DNAs [90–97].

In the last approach, the bottom-up and top-down methodologies are combined to realize more sophisticated nanomaterials. First, initial nanomaterials in the form of film or nanostructures are synthesized by a top-down method. Next, initial nanomaterials are further broken down by bottom-down techniques such as wet etching and dry etching. The development of the approach is still in an early stage and there are not many examples of nanomaterial syntheses based on this concept. The first example is anodized alumina (AAO) nanoporous thin film fabricated by the deposition of aluminum thin film and electrochemical anodization in phosphoric acid. The nanopore structure can be used for subsequent bottom-up growth of nanowires [98–101]. Similarly, nanoporous silicon thin film can also be made by sputtering of amorphous silicon layer and electrochemical or plasma etching [102]. Another notable example is the fabrication of graphene sheet from CNTs. CNTs synthesized by CVD process were etched along their sidewall by photoresist masking and oxygen plasma etching [103]. Another interesting example is silver nanowire formed by laser shock on silver thin film [13].

The most important aspect of nanomaterials is their special properties associated with nanoscale dimensions. The most fundamental characteristic of nanomaterials is the high surface-area-to-volume ratio, which results in a number of unusual physical and chemical properties such as high molecular adsorption, large surface tension force, enhanced chemical and biological activities, large catalytic effects, and extreme mechanical strength [104–106]. Another unique property of nanomaterials is the quantum size effect that leads to their discrete electronic band structure like those of molecules. Unlike the increased surface-to-volume ratio that also occurs when going from macro to micro dimensions, quantum effect is only specific to deep nanoscale dimension of smaller than a few tens of nanometer [107, 108].

The nanomaterials are thus highly useful for a wide range of nanotechnology fields including nanoelectronics [108–110], optoelectronics [109], nanophotonics [111–114], nano-electromechanical systems (NEMS) [115], bioelectronics [116], nanobiotechnology [117, 118], nanochemistry [119], biochemistry [120, 121], biomedicine [122–124], electrochemistry [125], nanomechanics [126, 127], and so on. These lead to a large variety of applications such as quantum-effect lasers/solar cells/transistors [128, 129], photonic band gap devices [113, 114], catalyst [130, 131], photocatalyst [132, 133], molecular electronic device [8], surface-enhanced Raman spectroscopy (SERS) [134], nano fuel cells [135, 136], nano drug delivery systems [41, 137], nanosensors [20, 25, 138, 139], advanced energy storage devices [140–142], and nanoactuators. Among these, sensors are among the fastest-growing applications due to their huge demands in many real-world application fields such as automobiles, communication, consumer electronics, industrial, and biomedical. Sensors can be divided into several classes including mechanical, thermal, optical, magnetic, gas, chemical, and biological.

Among various kinds of sensors, gas/chemical/biological sensors can exploit the most benefits from high surface-to-volume-ratio property of nanomaterials [143, 144]. Gas/chemical/biological sensors generally comprise sensing material that responds to changes of gas/chemical/biological analytes and transducer that converts the changes into electrical signals. Gas sensor may be classified by sensing mechanisms into chemoresistive, surface acoustic wave (SAW), quartz crystal microbalance (QCM), chemiluminescent, optical absorption, and dielectric types [145–149]. Gas-sensing applications include toxic gases such as NO_2, CO, SO_2, NH_3, O_3, and H_2S; flammable gases such as H_2, CH_4, C_2H_2, and C_3H_8; and volatile organic compounds (VOCs) such as ethanol, acetone, methanol, and propanol [146–150]. Similarly, chemical sensors can be divided by sensing platforms into electrochemical, ion-sensitive field effect, chemiluminescent, optical, and mass spectroscopic ones [151–153]. Chemical sensing applications are much wider than gas-sensing ones as they include a large number of liquid-phase chemicals ranging from acids, bases, solvents, and inorganic substances to organic analytes [154]. Likewise, widely used biosensing platforms include electrochemical, fluorescent, surface plasmon resonance (SPR), QCM, and microcantilever [20, 155–158]. Biosensing applications also cover a very broad range of biologically relevant materials including bioanalytes found in living organisms such as glucose, cholesterol and uric acid, DNAs, RNAs, cells, proteins, organelles, and so on [12, 157–160].

The main and common requirement of these sensors is high sensitivity and specificity. The specific surface area of sensing material is one of the most important factors that dictate the sensitivity as it directly related to adsorption or reaction rate with target analytes [161]. Gas/chemical/biological sensors developed based on well-established microtechnology are now currently used in commercial applications. They provide good sensitivity and reproducibility along with low power consumption. However, their performances are still not satisfactory for many advanced applications that involve detection of very low concentration analytes. The use of nanomaterials in these sensors will provide substantial improvement of sensing performances due to several orders of magnitude increase of specific surface area and smaller size [162–164]. Well-controlled synthesis and fundamental understanding of properties of nanomaterials are very important for the advancement of nanomaterial-based gas/chemical/biological sensors.

Recently, there has been significant progress in development of nanomaterial-based sensors. A wide variety of nanostructured materials and composites have been devised on different sensing platforms by a number of preparation methods for various sensing applications. For instance, high-sensitivity chemoresistive gas sensors based on metal oxide nanostructures such as SnO_2 nanowires, ZnO nanotetrapods, and TiO_2 nanorods have been extensively explored [144]. In addition, highly sensitive electrochemical biosensors based on the combination of biofunctional materials such as enzymes, antibody and DNAs, and novel electrode materials such as carbon/metal/conductive polymer/metal-oxide nanostructures, and nanocomposites such as CNTs, graphene, gold nanoparticles, CNTs/polyaniline, CNTs/ZnO, CNTs/gold nanoparticles graphene/polythiophene and alike are of great interest [12, 165, 166]. This book includes recent progress of selected nanomaterials over a broad range of gas/chemical/biological sensing applications and it is organized as follows.

In Chap. II the use of biofunctional nanomaterials in signal amplification for ultrasensitive biosensing has been discussed. The biofunctional nanomaterials with the abilities of specific recognition and signal triggering can be employed as not only excellent carriers, but also electronic and optical signal tags to amplify the detection signal. Two approaches including noncovalent interaction and covalent route for the functionalization of nanomaterials with biomolecules are described. The performance in terms of sensitivity and specificity are also digested.

In Chap. III, nanomaterial-based electroanalytical biosensors are reported and emphasized for cancer and bone disease diagnostics. The existing biosensor technologies, the mechanisms and applications of two types of electroanalytical biosensors and advantages of nanomaterials in developing these biosensors are described. Then, new nanomaterial-based electrochemical impedance biosensors applied in cancer and bone disease studies that can detect in real time without any pre-labeling-specific biomolecules at previously unattainable ultra-low concentrations are specifically discussed.

Chapter IV deals with CNT-based chemical and biosensors and its integration to microfluidic systems. Different components necessary for the construction of a microfluidic system including micropump, microvalve, micromixer, and detection system utilizing CNT-based electrochemical sensors are extensively surveyed and discussed.

Chapter V covers a comprehensive review of graphene-based chemical and biosensors. These include graphene's synthesis methods, properties, and different types of chemical and biosensors including chemoresistive, electrochemical, and other sensing platforms. In addition, concluding remarks for further development of graphene-based chemical and biosensors are provided.

In Chap. VI, molecularly imprinted polymers (MIPs) for sensing and diagnostics of various biological species are expansively reviewed and analyzed. The design of novel artificial MIPs and the limitations of the classical non-covalent imprinting approach are discussed. Some novel strategies for the molecular imprinting of macromolecules such as the use of complementary functional monomers and a new electrochemical approach to the imprinting of peptides and proteins as well as new concepts for the integration with transducers and sensors are described.

Chapter VII reports design, synthesis, fabrication, properties, and biomedical diagnosis applications of nanometal structures including Au and Ag nanoparticles (NPs) based on localized surface plasmon resonance (LSPR) biosensor platform. The characteristics including enhanced sensitivity, label-free detection capability, specific changes in their absorbance responses upon binding with various molecules are demonstrated and discussed.

In Chap. VIII, DNA sensors (genosensors) employing nanomaterials for diagnostic applications are extensively described. These DNA sensors employ electrochemical impedance principle to detect hybridization of a target clinical diagnostic-related gene with the complementary probe genes with no labeling. The use of nanocomponents to improve sensor performance, mainly CNTs integrated in the sensor platform, or nanoparticles, for signal amplification and their diagnostic applications will be reviewed.

Chapter IX describes novel nanoprobes for in vivo cell tracking used for evaluating the therapeutic efficacy by measuring the changes in tumor volume and tumor markers after cell-based immunotherapy. Various molecular probes and imaging modalities including intrinsic or extrinsic therapeutic cells' modification with proper molecular probes and in vitro amplification as well as recent advances in molecular imaging probes are discussed. Their application in relation to in vivo tracking of dendritic cells (DCs), natural killer (NK) cells, and T cells are then addressed.

Chapter X includes optical chemical gas sensor and electronic nose based on optically active organic nanomaterials made of metallo-porphyrin (MP) and metallo-phthalocyanine (MPc). The gas-sensing mechanism, preparation methods of sensors, the optical absorption spectral measurement under ambient conditions, and application to electronic nose with principal component analysis (PCA) are described.

In Chap. XI, the uses of nanotechnology to attain highly sensitive detection in electrochemical microdevices are reviewed. Issues relating to miniaturization of electrochemical electrode and system are discussed. Various techniques applicable to fabrication and integration of nanoelectrodes are included.

2 Perspective of Nanomaterial Development for Sensing Applications

The development of nanomaterials for sensing applications is still in an early stage and there remains much more work to be done and some challenging issues to be overcome before nanomaterials can successfully be commercialized. Novel functional nanomaterials and new synthesis methods are still being further explored to achieve sensors with ultra-high sensitivity. Among novel nanomaterials, graphene and its composites are especially promising and their research in sensing applications has been growing tremendously [167–169]. Moreover, several nanomaterials have not yet been studied in many gas/chemical/biological applications due to application diversity, and these explorations are highly needed. Among these, new biological sensing applications such as virus-causing newly born infectious diseases and dangerous diseases such as cancer are of particular interest [170–172]. In addition, nanomaterials have not yet been applied in several sensing platforms to optimize their sensing capability. Thus, the integration of nanomaterials in novel sensing platforms such as plasmonic-based sensors is another important research direction [173, 174]. Furthermore, nanomaterial-based sensors should be integrated into processing systems such as microfluidics or lab-on-a-chip so that sample preprocessing and analysis can be automated. Presently, only some nanomaterial-based sensors have been successfully embedded in microfluidic devices [175–177]. Thus, fabrication of microfluidic devices with integrated nanomaterial-based sensors should be further developed.

One of the most important problems of nanomaterial-based sensors is their poor reproducibility because it is difficult to control the structure and arrangement of nanomaterial on sensor. Highly controlled synthesis and manipulation of nanomaterials are still major technological challenges [178]. Therefore, highly ordered nanomaterials and their implementation in sensing platforms are among the most important research topics in nanomaterials [179]. This leads to a new research field, namely *Nanoarchitectonics*, which is a conceptual paradigm for design and synthesis of dimension-controlled functional nanomaterials [180]. Self-assembled processes for various nanomaterials and structures are the most promising keys to achieve these nanostructures [46, 181–183]. However, effective methods and supporting instrumentation are still lacking and require significant technological development such as novel methods for arbitrary guiding assembly [184–187].

Another potential difficulty is high mass manufacturing cost due to sophisticated processing and instrumentation. Thus, development of fabrication process for low-cost and well-controlled large-scale nanostructure in sensing devices is another important future research topic. Chemical route syntheses [188–190] and printing techniques [191, 192] such as inkjet, gravure, and screen printing on low-cost, flexible substrates such as polymers and paper are among potential solutions to realize low-cost and disposable nanomaterial-based sensors, and research in this area should earn particular attention. Moreover, the integration of flexible and printed nanosensors with organic and printed electronics (OPE) for full functional sensing devices and systems will be a very active research field due to their important applications in smart textile, smart clothing, smart paper, and so on [193].

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Signal Amplification Using Nanomaterials for Biosensing

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Abstract Signal amplification based on biofunctional nanomaterials has recently attracted considerable attention due to the need for ultrasensitive bioassays. Especially, most nanoscaled materials are biocompatible, which permits them to act in direct contact with the environment as carriers of biological recognition elements for obtaining lower and lower detection limit. In order to achieve the good performance for biosensing, two approaches including noncovalent interaction and covalent route have been introduced for the functionalization of nanomaterials with biomolecules. The biofunctional nanomaterials with the abilities of specific recognition and signal triggering can be employed as not only excellent carriers, but also electronic and optical signal tags to amplify the detection signal. These advantages provide a new avenue to construct a sensitive and specific platform in nanobiosensing.

Keywords Biosensing, Functionalization, Nanomaterials, Signal amplification

Contents

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1 Introduction

The need for ultrasensitive bioassays and the trend towards miniaturized assays make the biofunctionalization of nanomaterials become one of the hottest fields [1, 2]. These biofunctionalized nanomaterials can be used as carriers or tracers to obtain the amplified detection signal and the stabilized recognition probes. Based on the unique properties of nanomaterials, the biofunctional nanoparticles can produce a synergic effect among catalytic activity, conductivity, and biocompatibility to result in significantly signal amplification for designing a new generation of nanobiosensing device.

A lot of nanomaterials, such as metal nanoparticles, carbon-based nanostructures, and magnetic nanoparticles have been introduced as carriers for the signal amplification. In particularly, carbon-based nanomaterials and metal nanoparticles show to promote the direct electron transfer between the biomolecules and electrode surface. For example, based on excellent conductivity, the single-walled carbon nanotubes (SWNTs) can act as a nanoconnector that electrically contacts the active site of the enzyme and the electrode with the interfacial electron transfer rate constant of 42 s^{-1}, which provides a significant potential for constructing an electrochemical biosensor [3]. Using superparamagnetic particle as carrier for signal amplification, surface plasmon resonance (SPR) immunoassay has been achieved for the detection of cancer biomarker prostate specific antigen (PSA) in serum at an ultralow detection limit of 10 fg mL^{-1} [4].

As a signal trace, the biofunctionalized nanomaterials have the abilities of specific recognition and signal amplification in optical, electrochemical, and photoelectrochemical assays [5, 6]. In optical assay, nanoparticle probes such as fluorescence energy transfer nanobeads and quantum dots (QDs) provide significant advantages of signal brightness, photostability, wide dynamic range, and multiplexing capabilities comparison with organic dyes and fluorescent proteins. Electrochemical assays based on nanoprobes are attractive because of their low cost, high sensitivity, simplicity, and easy miniaturization. The electrochemiluminescent (ECL) and photoelectrochemical assays hold the advantages of both optical and electrochemical detections are a promising perspective.