A Brief Review on the Application of Gold Nanoparticles as Sensors in Multi Dimensional Aspects

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Abstract: The presence of chemical toxins, heavy metals, inorganic and organic pollutants in water, biological toxins and even pathogens due to either natural or artificial processes (Duan et al. 2007, Wang et al. 2010), needs to be monitored constantly and continuously in order to safeguard the supply of clean potable drinking water to the public, and to control the impact on the environment and the ecosystem. In recent years, the combination of nanotechnology along with the basic sciences of chemistry, physics and biology, has allowed the development of ultrasensitive detection and imaging methods, including applications in electronic, magnetic, environmental, pharmaceutical, cosmetic, energy, optoelectronic, catalytic and material fields (Auffan et al. 2009, Wang and Ma 2009, Wang et al. 2010). This can be sorted and solved by the application of gold nanoparticles (AuNP) - based sensors that have the potential to detect toxins, heavy metals, and inorganic and organic pollutants in water rapidly with high sensitivity and play an increasingly important role in environmental monitoring.

I. Introduction

Environmental monitoring is becoming increasingly alarming to protect the public and the environment from toxic contaminants and pathogens released into air, soil, and water from toxic chemical wastes, spills, manufacturing waste and even underground storage tanks. The United States Environmental Protection Agency (U.S. EPA) has thoroughly imposed strict regulations on the maximum allowable concentrations of many environmental contaminants in air and water and is reported to be monitoring over two million underground storage tanks containing hazardous (and often volatile) contaminants from as early as 1992. Nanotechnology has the potential to suggest solutions to minimize or eliminate the use of toxic materials and the generation of undesirable byproducts and also to sensitively detect (and monitor) specific polluting agents well before any major environmental disaster occur. Researches related to improved industrial processes and starting material requirements, development of new chemical and industrial procedures and materials to replace current hazardous constituents and processes resulting in reductions in energy, materials, and waste generation are being supplemented by the application of nanotechnology to control and predict the potential damage to the environment.

For the past one and a half decade, the field of environmental monitoring has seen the application of nanoparticles (NPs) being utilized as the functional probes for analyzing toxins, metal ions, and inorganic and organic pollutants (Cheon and Lee 2008, Wang and Ma 2009). NPs, usually within the size 1 and 100 nm, display unique properties not fou
nanotechnology because of their electronic, optical, catalytic and thermal properties. Amongst these, gold nanoparticles are intensively used in a variety of colorimetric and fluorescence biodetection assays. Specific focus has been directed at colloidal gold nanoparticles ranging from 3 to 100 nm in size, since they are rather stable and their properties can be easily amended by chemical modification of their surfaces.

Metal nanoparticle sensors should be field-portable, inexpensive, rapid, reliable and usable without technical training. Certain non-molecular chromophores such as free-electron metal (e.g., gold, silver, copper) nanoparticles, however, can display visible-region extinction coefficients that are up to several orders of magnitude higher than even the most intensely coloured conventional molecular dyes [4].

Noble metal nanoparticles such as silver (AgNPs) and gold nanoparticles (AuNPs) have attracted remarkable interest in the past few years as they exhibit strong absorption of electromagnetic waves in the visible region due to surface Plasmon Resonance (SPR), highly stable dispersions, chemical inertness, and biocompatibility. A small change in the NPs size, shape, surface nature, and distance between particles leads to tunable changes in their optical properties which draws application in the fabrication of optical devices, catalysis, surface-enhanced Raman scattering (SERS), bioimaging, colorimetric sensors, and so on. Amino acids (AA) are usually classified in different ways based on the polarity and nature of side groups; namely, weakly acidic or basic, hydrophilic, and hydrophobic. The physicochemical properties of the side groups are important because they can influence the reduction, stabilization, and conversion of reducible metal ions (Ag+/Au3+) to the NPs, respectively.

Polymer capping of nanoparticles serves a two-fold purpose, that of stabilization and surface functionalization for applications as sensors. Further modification of the attached alginate molecules has the promise to achieve high specificity sensors for various applications. Apart from applications in colorimetric pollution sensors, alginate capped gold nanoparticles may have biology-oriented applications because it was found that alginate shows selectivity in attachment to certain kinds of bacteria [5].

When heavy metal ion is added to gold nanoparticle capped with polymer, functionalized group in polymer attaches with metal ion leading to the shape and size of nanoparticles being changed, resulting in a change in surface plasmon resonance frequency. A comparison of the optical absorption spectra of the colloidal suspension before and after exposure to metal ions is a good indicator of the concentration of the heavy metal ions. Optimization of the deconvolution of the optical absorption spectra gives a fantastic tool to follow the agglomeration process of gold nanoparticle through the chelation of the cations on the polymer utilized for the steric stabilization that has been used for ion-sensing. In order to complete the chelation of the metal ions like copper, zinc and manganese, about 1 hour was sufficient to complete the reaction in most of the cases. This simple metal ion sensor can be implanted in lab-on-chip type of applications for easier implementation [6].

The wide variation of optical properties of metal nanoparticles with particle size and shape, particle–particle distance, and the dielectric properties of the surrounding solution due to the phenomenon called surface plasmon resonance enables construction of simple but sensitive colorimetric sensors for various analytes. The chemical inertness and resistance to surface oxidation make production of gold nanoparticles easier in comparison to other metal nanoparticles.

The dependence of the plasmon band position on the degree of aggregation of the nanoparticles and on the dielectric constant of the local environment forms the basis for chemical sensing with gold nanoparticles. The presence of chemical or biological analytes can induce aggregation, disaggregation, or change the local refractive index, which accordingly results in change of the plasmon band position (for a review on the chemical sensing using gold nanoparticles see Murphy et al. 2008a) [7].

Surface-modified nanoparticles, such as gold and silver NPs (AuNPs/AgNPs) (Yu and Irudayaraj 2007, Xiao and Yu 2010 Wang and Yu 2012), quantum dots (QDs) (Peng et al. 2000, Peng and Peng 2001, Qu et al. 2001), magnetic NPs (MNs) (Sun et al. 2006, Aurich et al. 2007, Kim et al. 2007, Taktak et al. 2007, 2008, Koh et al. 2008, Lowry et al. 2008) and carbon nanotubes (Shim et al. 2008, Zhang et al. 2010) can have specific target-binding properties that allow highly selective and sensitive target detection. As shown in Figure 1(Peng et al. 2009), different types of NPs demonstrate different optical, fluorescence and magnetic properties, and interactions between these properties give NPs great potential for environmental screening.

In this article, we also focus on the application of AuNPs on the detection of waterborne chemical and biological pollutants. The unique optical properties of AuNPs come from the collective oscillation of electrons at their surfaces, known as surface plasmon resonance (SPR). Surface plasmons (SPs) are coherent electron oscillations that are excited by electromagnetic (EM) radiation at the metal-dielectric interface. The characteristics of such light-metal interactions are determined by the properties of the metal, the dielectric environment, and the frequency of the EM radiation. When the frequency of the SP resonates with that of the
excitation radiation, SPR will occur at the metal-dielectric interface (Maier SPR will occur at the metal dielectric interface (Maier and Atwater 2005, Ozbay 2006, Atwater 2007). The SPR frequency is determined by the size, shape and chemical composition of the metallic NPs.

For spherical AuNPs, the resonance frequency lies in the visible region of the electromagnetic spectrum (Maier and Atwater 2005). Since AuNPs have a high surface area-to-volume ratio, the SPR frequency is exquisitely sensitive to the dielectric (refractive index) nature of its interface with the local surrounding medium (Wang et al. 2010). Any changes to the environment of these particles (i.e., surface absorption/desorption of chemical reagents, aggregation, medium refractive index, etc.) will shift the SPR frequency and result in a colorimetric change that can be utilized as signals for detection (Murphy 2002, Niemeyer and Simon 2005, Yu and Irudayaraj 2007). Detection schemes also often utilize the effect of enhancement on the local EM field surrounding the AuNPs caused by SPR. These enhancements, surface-enhanced Raman scattering (SERS) being one example, can lead to extraordinary sensitivity in chemical sensing; the detection level of a single target molecule has been reached in SERS (Kneipp et al. 2006). Further development in nanofabrication methodologies and sensor instrumentation will lead to much wider applications of these extremely sensitive nanosensors outside research laboratories (Lee and El -Sayed 2006, Stewart et al. 2008).

AuNPs have also been utilized in electrochemical sensing applications, where the AuNPs are deposited onto the surface of electrodes to improve the sensitivity of their electrochemical responses to the absorption of analytes (i.e., heavy metal ions, toxin species, etc.) (Dai and Compton 2006, Martínez Paredes et al. 2009 ). With the AuNP-induced enhancement to the electrochemical signalling, ppb level limits of detection (LOD) have been achieved for a variety of environmental pollutants (Dai and Compton 2006, Martínez-Paredes et al. 2009).

Gold nanoparticles can also be used as sensors. Their optical properties can change upon binding to certain molecules, allowing the detection and quantification of analytes. The absorption spectra of gold nanoparticles change drastically when several particles come close to each other. Another strategy for sensing makes use of fluorescence quenching. Fluorescent molecules that are excited and in close proximity to a gold particle can transfer their energy to the metal, resulting in a non-radiative relaxation of the fluorophore. In several different detection schemes the analyte displaces the fluorescent molecules from the particle surface or changes their conformation, so that the optical emission of those reporter molecules is changed in the presence of the analyte [8].

Applications of gold nanoparticles (AuNPs) as sensors are usually based on detecting the shifts in SPR peak, due to either change in the dielectric constant around the nanoparticles as a result of adsorption of analyte molecules, or due to the analyte- induced agglomeration of the gold nanoparticles.

To date, the SPR frequency of Au NPs has been shown to depend on particle size, shape, dielectric properties, aggregate morphology, surface modification, and refractive index of the surrounding medium. For example, the SPR peak of 13 nm spherical gold colloids is around 520 nm and that of 5–6 nm silver NPs around 400 nm.

The gold nanoparticles are stabilised by physical adsorption of excess anions (citrate ions) in the solution medium. Hence, such colloidal suspensions are very sensitive to the change in concentration of ions in the solution. The chemical inertness and resistance to surface oxidation make production of gold nanoparticles easier in comparison to other metal nanoparticles.

II. Detecting Heavy Metal Ions

The development of precise and sensitive metal ion sensors has always been a major research thrust in academics and healthcare. The reason is simple; we need a sensor system that we can use to provide on-site and real-time monitoring of toxic metal ions (Pb2+, Cd2+, Hg2+, and Se2+) in applications such as industry waste monitoring, environmental biology, and clinical toxicology. In general, a simple colorimetric sensor is preferable because the cost can be minimized and they can be made for portable real-time detection. Furthermore, a metal ion sensor with a tunable dynamic range is desirable for applications in widely different concentration ranges. So far, many approaches have been reported to widen the dynamic range without having to design new sensors. Here, we describe various designs of metal ions sensors based on Au NPs setup and their use for sensitive and selective detection and quantification of metal ions [9].
Heavy metals like Li+, Na+, K+, Mg2+, Ca2+, Ba2+, Ni2+, Cu2+, Fe2+, Fe3+, Cr6+, Zn2+, Co2+, Cd2+, Pb2+, Cr3+, Hg2+, and Mn2+ are reported to be potential environmental pollutants as many of them are toxic even at trace ppm level concentrations. Therefore, determination of toxic metals in the biological system and aquatic environment has become a vital need for remedial processes. So far, there are several reports available for the detection of heavy metal ions using various analytical instruments. During recent years, AgNPs and AuNPs have been extensively used for colorimetric detection of heavy metal ions due to their tunable size and distance-dependent optical properties with high extinction coefficients at the visible region. Advantages of using NPs as colorimetric sensors are proven to be a promising approach for simple and cost-effective protocols with high sensitivity and rapid tracking of valuable and toxic metal ions in environmental samples/systems. So far, there are several reports available for the detection of environmentally toxic metal ions (Hg2+, Pb2+, and Mn2+) using NPs of metal ions. For instance, Wang et al. reported the detection of Hg2+ ions with the naked eye using unmodified AgNPs and mercury-specific oligonucleotides as sensors. Senapati et al. reported detection of Hg2+ using popcorn-shaped gold nanoparticles protected by tryptophan as a probe with selectivity. Recently, Farhadi and co-workers reported the use of green synthesized and unmodified AgNPs for Hg2+ detection. Chai and co-workers reported colorimetric detection of Pb2+ using glutathione functionalized AuNPs. AuNPs generated through sunlight irradiation were used as an ultrasensitive probe for the detection of Pb2+ ions. Metal nanoparticles have been utilized for naked eye detection of lead ions in aqueous media. Recently, Zhou and co-workers reported colorimetric detection of Mn2+ using AgNPs cofunctionalized with 4 mercapto benzoic acid and melamine as a probe. The prepared NPs are characterized using various instrumental techniques and are found with good water dispersibility, biocompatibility, and stability up to six months. Also, they offer the possibility to be a potential colorimetric sensor for the detection of Hg2+, Pb2+, and Mn2+ ions in aqueous medium.

Calixarene functionalized gold nanoparticles (CFAuNPs) have been prepared and characterized by spectroscopic and microscopic (TEM) techniques. To use this material as potential colorimetric sensor, the binding property of this new material has been investigated with a large number of metal ions. It exhibited sharp colour change from dark brown to green and blue, detectable by naked-eye, in the presence of Cu2+ and Pb2+ ions, respectively. It has also triggered substantial change in surface plasmon resonance (SPR) band of the functionalized gold nanoparticles, which in case of Pb(II) is due to the inter particle plasmon coupling arising
Detection of bacterial pathogens: The second immunological detection system is based on the aggregation of antibody functionalized gold nanoparticles with bacteria. Gold nanoparticles are characterised by their intensive light absorption which is caused by excitation of collective oscillations of valence band electrons, called plasmon resonance. The plasmon resonance wavelength is, amongst others, a function of the direct particle environment so that changes therein can be monitored spectroscopically [12].

Gold nanoparticle-based probes have been used in the identification of pathogenic bacteria in a chip-based system. The assay consists of a capture DNA strand immobilized on a glass chip that recognizes the DNA of interest. A separate sequence on the captured target strand is then labelled with an oligonucleotide-functionalized gold nanoparticle probe. After catalytic reduction of silver onto the gold nanoparticle surfaces to amplify the target signal, the capture-strand/target/nanoparticle sandwich is visualized with a flatbed scanner. The assay depends upon the target-selective binding of gold nanoparticle probes to consecutive regions of a target DNA sequence in solution, followed by transfer to an evanescently illuminated glass microscope slide for light scattering measurements. Whereas the gold particle probes scatter orange light in the presence of target, the probes scatter green light if the target is absent, whilst the target concentration is quantified by measuring the intensity of scattered light. Multiplexed detection of different viruses and bacteria, using gold nanoparticles surface functionalized with a target-specific oligonucleotide and further encoded with a Raman-active dye molecule, has also been demonstrated. Whereas the complementary probe sequence imparts the specificity for the target sequence of interest, the presence of the target is confirmed by silver staining and the identity of the target is revealed by detecting the surface-enhanced Raman scattering (SERS) of the Raman dye near the
nanoparticle surface. This assay demonstrated a sensitivity of 1 fm target concentration.

Despite its widespread use in nucleic acid hybridization assays, the use of gold nanoparticles for detection of bacterial pathogens in immunoassays has only recently been described. The assay comprises detection of organism-specific antigens with biotinylated polyclonal antibodies after which gold particles functionalized with a secondary antibiotin antibody are added, and the particles are then visualized under a dark-field stereomicroscope. The immunoassays were demonstrated to reliably detect Helicobacter pylori and E. coli O157:H7 antigens in quantities in the order of 10 ng, which provides a sensitivity of detection comparable to those of conventional dot blot assays. A two dot filter system has also been developed where colloidal gold nanoparticles (2 nm) were bounded onto anti-E.coli O157:H7 antibodies. These monoclonal antibodies were bounded onto a 0.2 microm nitrocellulose filter membrane through which water was filtered. The same antibodies that captured the bacteria acted as detectors since the gold nanoparticles could be visualized under epifluorescence. This one-step detection method not only had a low detection rate (1 cfu/100 ml) and high specificity but would be inexpensive and easy implemented in the routine testing of water samples.

Gold Nanomaterial-Based Sensing of Biological Toxins from Food Samples: Water and food pollution caused by food pathogen contamination is a serious problem in the world. Very often, concentrations of pathogens in food contamination are very small and on the other hand, the number of different possible pathogens is high. As a result, it is not easy to test pathogens in every food sample collected. The goal of this project is to develop gold-nanoparticle based absorption spectroscopy assay for ultrasensitive and highly selective detection of pathogens in water and food samples. The REU students will be involved in synthesis and characterization of different gold nanoparticles, surface modifications with antibodies, and finding its use as plasmon sensors for pathogens.

IIIIII. Conclusions and future perspectives

Environmental sensor research generates considerable interest and activity nowadays. In this review, we summarized the recent progress in AuNP synthesis, as applied to environmental sensing, and the use of AuNPs in the detection of environmental pollutants.

Over the past decade, advances in AuNP synthesis and fabrication have led to an explosion of both efforts and reports on the emerging field of AuNP-plasmonics. Significant progress has been made in creating novel nano-sized sensors for chemical and biological sensing and imaging. AuNP-based sensors provide promising approaches for selective and sensitive analyses, and have advantages over traditional instrumental analyses, as they are usually compatible with portable devices that can be deployed in field for onsite sample screening. With the advance of microfluidic sample handling units, this kind of portable device can be developed for multi-plexed, quantitative and rapid analysis, and can measure unprocessed field-collected water samples with a high sensitivity. High-throughput and ultrasensitive detection technology, based on AuNPs, offer effective screening methods for many environmental analytes. This technology will certainly find widespread applications in water quality and safety monitoring in the near future.

Researchers worldwide are actively exploring two lines of research: (1) new materials, such as anisotropic-shaped AuNPs, or Au alloy NPs, are being fabricated and new theories and models are being developed and investigated to expand our understanding of plasmonic phenomena at the nanoscale; and (2) new sensing instruments and/or platforms are being designed and exploited, based on the growing knowledge bases, to provide unprecedented sensitivity and resolution for chemical and biological sensing and imaging. These two lines of research are merging to yield next-generation nanosensors. However, it should be noted that a number of critical issues still need to be addressed before they can become realistic tools for environmental monitoring. Reliable manufacturing methods to produce AuNPs in a large scale, with good reproducibility, are still lacking, especially for anisotropic shaped particles; long-term health effects of nanomaterials still need to be characterized and a high throughput assay, which is very important for environmental applications, needs to be developed in field-deployable platforms. Nevertheless, we expect, in the near future, that increased collaboration between scientists from different disciplines will yield new fundamental insights into the AuNP-based nanotechnology and result in more powerful nanosensors for various applications.

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