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STUDY OF PLASMONIC NANO-MATERIALS FOR SURFACE-ENHANCED LOCALIZED SURFACE PLASMON RESONANCE SPECTROSCOPY (LSPR) &THEIR APPLICATIONS FOR OPTICAL ANTENNAS

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Abstracts: *The plasmonic properties of nanoparticles have attracted much attention in the Past decades .The plasmonic properties of nanoparticles having non cylindrical shape with triangular base. Two characteristics plasmon bands have been recoreded in absorption spectra. dielectric property of surroundings. The higher wavelength localized surface Plasmon resonance (LSPR) peak shifts to higher wavelength with an increase in the nanoparticle size. Their potential use in optical spectroscopy, photonic devices, biosensors, as well as in the waveguides makes them a very active area of research. The localized surface Plasmon resonance (LSPR) of such nanoparticles plays an important role in such applications. Localized surface plasmon resonance occurs when the electrons in the nanoparticles interact with electromagnetic radiation.Nanotechnology holds the promise of delivering the greatest technological breakthroughs in history.*

Keywords: *Plasmonic, Optical Nanoantennas, Localized Surface Plasmon Resonance, Nanophotonics, Biosensors, Spectroscopy, Nanoimprint lithography, Nanopore shaped, pattern, Protein array, Prostate specific antigen.*

Introduction: Plasmonics is an emerging branch of nanophotonics that examines the properties of the collective electronic excitations in noble metal films or nanoparticles known colloquially as surface plasmons [1-2]. The excitement of plasmonics lies in its potential to achieve highly miniaturized and sensitive photonic devices by controlling, manipulating, and amplifying light on the nanometer length scale Plasmonic nanoantennas provide new routes for efficiently detecting, analyzing, and monitoring single biomolecules via fluorescence, Raman, and infrared absorption spectroscopes [3-4]. The development of efficient biosensors for multispectral spectroscopy remains nevertheless limited by the narrowband responses of plasmonic devices, as they are generally designed to operate in a specific bandwidth, matching with the absorption, scattering, or emission frequency of target biomolecules under investigation [5-6]. Therefore, performing biosensing from visible to infrared frequencies systematically requires designing and fabricating multiple plasmonic nanoantenna configurations and prevents the development of nanoscale integrated sensors for multispectral probing of random chemical species [7-8]. From the presence of dead bacteria. Thus, various diagnostic biosensors based on nanotechnology have been recently developed for the sensing of low concentrations of biomolecules and the recognition of biomolecular interactions [9]. In general, a nanobiosensor is defined as a device that recognizes biological phenomena at the molecular scale with high affinity and specificity and subsequently transduces signals into quantifiable information [10-11]. Among the variety of nanobiosensors available, localized surface plasmon resonance-(LSPR-) based nanobiosensors are considered one of the most powerful tools in the biotechnology and biosensor fields here, we propose to overcome these limitations by using broadband log-periodic nanoantennas designed to generate significant electromagnetic intensity enhancements from the visible to the mid-IR wavelength regions [12]. I demonstrate simultaneous surface-enhanced fluorescence, Raman, and infrared absorption spectroscopies for biomolecules functionalized on top of single nanoantennas, which opens new opportunities for the development of integrated devices suitable for multispectral biosensing on the same chip [13]. Optical antennas (OAs) enable the control and manipulation of optical fields at the subwavelength scale, and thus hold promise for enhancing the performance of photodetection spectroscopy nano-lithography sensing etc. Due to the well-established radiowave and microwave antenna theories and structures, many structures in optical antennas for electric field enhancement, e.g. bowties, dipole antennas and split ring rings are introduced from their counterparts in radio wave and microwave region [14]. In addition to electric field enhancement, the OAs for enhancing the optical magnetic field in near field has drawn much attention recently due to its potential applications, such as magnetic sensor magnetic nonlinearity and magneto-optic modulation of Plasmon polaritons Recent works have shown that by applying the well-known Babinet's principle, magnetic field can be confined and enhanced in near-IR by means of the complementary structures of bowtie aperture antennas (BAA) or bowtie antennas (BA) called diabolo antennas (DA) or complementary bowtie apertures (CBA) As is well known, SRRs is one important structure for electric field enhancement and has been studied extensively, including many previous studies related to the extraordinary electromagnetic properties, e.g. the negative permittivity metamaterials, using arrays of SRR and their complements Of most interest, therefore, is to investigate that whether the complement of SRR can exhibit the same behavior as DA and CBA in enhancing and localizing optical magnetic field [15]. Light is ubiquitous and plays a very important role in our daily lives. The light we receive from the sun or light that we produce using artificial sources is invaluable for the perception of our surroundings Light refracts as it enters the lens in our eye, forming an image on the retina. Using lenses and mirrors in microscopes, telescopes and other optical equipment, have managed to improve the control of light the dispersion, which is the relation between the temporal and spatial frequency of light [16]. Conventional optical materials have a refractive index that is roughly independent of frequency over the visible wavelengths**.**

1. A Localized Surface Plasmon Sensor: Application of surface plasmon technology is widespread in sensing Surface plasmon resonance (SPR) sensors are commercially available and use a metal coated prism in the reflection geometry. Nanoscale metallic antennas couple incident optical beams to length scales much smaller than the diffraction limit at optical frequencies. By probing variations in the angle/wavelength dependent reflection due to the excitation of surface Plasmon polaritons on the metal film, the refractive index of an analyte at the surface is sensitively measured. One major disadvantage of the prism-based geometry is that it is bulky as it relies on the measurement of a surface plasmon that propagates over a relatively large distance and that relatively large amounts of analyte are required. To solve this problem, the sensor can be based on plasmons confined to metallic resonators in which light at the cavity resonance frequency is recirculated in a small volume. Such localized surface plasmon resonance (LSPR) sensors hold promise for devices with an intrinsically small footprint and offer a range of possible applications in miniaturized geometries, nanofluidics and multiplexing arrangements. The resonance of an LSPR sensor undergoes a spectral shift as a result of a change in the refractive index of the surrounding medium. A measurement of this shift, for example by recording the scattered intensity at a certain wavelength, is thus a sensitive probe of the refractive index change The figure of merit for the sensitivity is defined as $\Delta\lambda/(\Delta n W)$ with $\Delta\lambda$ the spectral shift as a result of index change Δn of the resonance with spectral full-width-at-half-maximum W. A side from having a high an effective geometry must also be integrable with read-out optics Among the variety of nanobiosensors available, localized surface Plasmon resonance-(LSPR-) based nanobiosensors are considered one of the most powerful tools in the biotechnology and biosensor fields. LSPR possesses the specific characteristics of metallic or metalized nanostructured materials, such as precious metal nanoparticles, which can be excited by irradiation with incident photons and is resonant with the collective oscillations of conduction electrons at a specific wavelength. the peaks of LSPR-related spectra are sensitive to the dielectric medium on the surface of the precious metal nanoparticles that can be used to recognize biomolecules In particular, nanobiosensors based on LSPR have the following advantages for the detection of biomolecules high sensitivity via detection of refractive index changes, no labeling requirement because of sensing of spectral shifts real-time assay accessibility using micro- fluidic systems good reproducivity.

2. Single Molecule Raman Spectroscopy Using Optical-Nanoantennas: Obtaining the Raman spectra of single molecules is a challenging task, due to the fact that Raman cross sections are very small. It is for this reason that reports of single molecule SERS were received with considerable attention. reports that followed, however, have, with the exception of employed the salt-induced aggregation of Ag colloids to generate the necessary SERS substrates. The problem is that these aggregates are very heterogeneous and usually fewer than 1 in 100 are active. This motivates the development of highly controllable plasmonic nanostructures for a single optical antenna was fabricated, and was reported, based on the bianalyte technique with Here, I describe recent work in which I have demonstrated using chips containing more than one thousand optical antennas. The Optical nanoantennas based on metallic nanostructures sustaining localized Plasmon resonances can allow to controlled delivery of far-field radiation to near-field hot spots of electromagnetic energy, and are hence a powerful platform for surface enhanced spectroscopies. I have calculated the decay rates and antenna efficiency of an electric dipole emitter coupled to these optical antennas. I first found the right orientation and position of the electric emitter which can radiate the local energy to the far field, cause huge emission enhancement, and have high antenna efficiency. I then perform the far field analysis of both efficiency of single molecule sensitivity was achieved was proven using isotopologue implementation of the bianalyte technique of the same molecule, at concentrations three orders of magnitude lower than that of Statistical analysis of the results revealed that a near-unity fraction of the antennas had single molecule sensitivity. We furthermore directly measured the angular emission patterns at the single molecule level using the EMS technique.

3. Nanoparticle Preparation & Fabrications: Nanoparticles play an important role in the metabolism and functioning of living organism.NSL was used to fabricate monodisperse, surface-confined Ag and Au nanoparticles.For these experiments, single-layer colloidal crystal nanosphere masks were prepared by drop coating ~2µL of nanosphere solution onto glass substrates. Once the nanosphere masks were dry, the substrates were mounted into a Consolidated Vacuum Corp. vapor deposition system. A Leybold Inficon XTM/2 quartz crystal microbalance (East Syracuse, NY) was used to measure the thickness of the Ag or Au film deposited over the nanosphere mask. The in-plane width (or perpendicular bisector) of the nanoparticles was varied by changing the nanosphere diameter used in the NSL process. Following metal deposition, the nanosphere mask was removed by sonicating the sample in ethanol for 3 min. The samples were either thermally annealed

4. Ultraviolet-Visible Extinction Spectroscopy: All spectra collected are macroscopic measurements performed in standard transmission geometry with unpolarized light. The probe beam diameter was approximately 2 mm.

5. Optical Detection Systems Based on Plasmon Nanoparticles: Recent growth in the field of highly sensitive optical transducers has captured the interest and led to the development of various optical biosensors in diverse fields ranging from clinical diagnostics to therapy. Interestingly, recent highly advanced and newly developed optical detection systems are mostly based on the surface Plasmon mechanism. Surface Plasmon resonance (SPR) is found in materials that have a negative (real) and small positive (imaginary) dielectric constant, especially in noble metals. When exposed to light, it is trapped near the surface as it interacts with the plasma of electrons near the metal surface. The resonant interaction between electron-charged oscillations near the surface of the metal and the electromagnetic field of the light creates the surface Plasmon. Generally in surface Plasmon-based detection systems, either propagating surface Plasmon polarition or non-propagating localized surface plasmon resonance (LSPR) are used. The surface Plasmon polarition can be excited on the thin metal surface by light coupled with gratings or prisms. This Plasmon propagates along the metal surface and the dielectric interface until the energy is lost or absorbed. Changes in the refractive index on the metal surface affect the plasmon resonance conditions, and can be measured by intensity changes, wavelength or angle shifts. Comparably, when surface plasmons are confined to a nanomaterial which is much smaller than the wavelength of light, it is localized around the nanostructure with a specific frequency known as the LSPR. The spectral characteristics of the non-propagating LSPR are independent of size, shape, composition, and the local dielectric environment, therefore, the refractive index changes induced by an adsorbate on a metal nanostructures can be used to monitor molecular binding events.

A few studies on the development of detection systems based on the LSPR mechanism to detect viruses such as hepatitis B (HBV) and swine origin influenza A (H1N1) have proposed a simple electrochemical deposition technique to fabricate highly ordered circular shaped Au nanopatterns on a transparent indium tin oxide (ITO) substrate and applied it for HIV virus detection based on the LSPR mechanism (Figure 1.(i).I have developed a more improved system with gold nanoparticles is able to capture& detect infected patient whole blood samples and also showed the integration with a microfluidic system with an optical photonic crystal (a TiO2 coated polymer nanostructure) in a microwell system.

The presence of HIV virus particles was measured through absorbance changes, which resulted from the change in refractive index on the Au surface with specific binding occurring through immunoreactions without any labeling materials. Since optical detection systems based on the LSPR mechanism have various advantages such as rapid preparation, high sensitivity and selectivity, they could be a promising detection system to monitor and treat the disease.

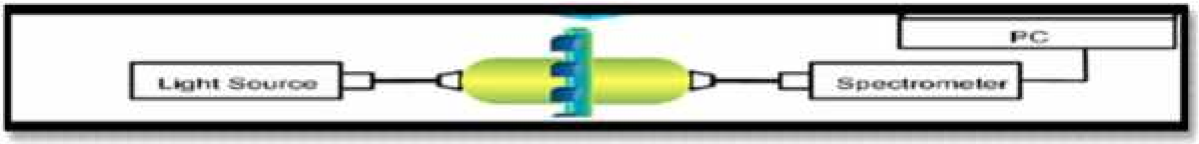

Fig.1 (i) Optical detection of HIV-1 virus based on LSPR mechanism. The configuration with LSPR method to detect the particles of HIV-1 using this technique for optical detection of virus

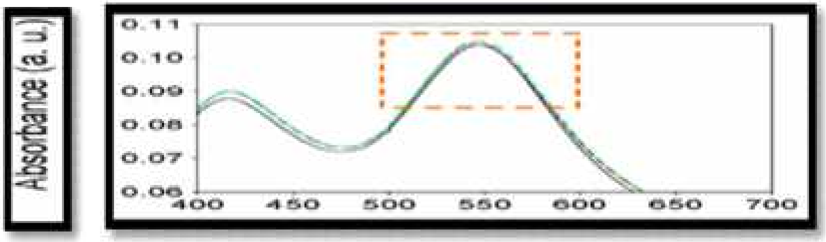

Fig1 (ii) Optical characteristics of peak based on the: (**a**) bare Au nanopattern on ITO substrate

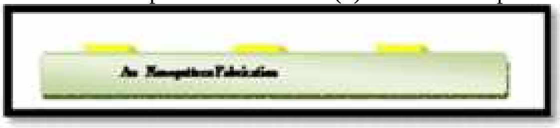

Fig1 (iii) Au Nanopattern Fabrication of Nanopore Shaped Patterns on Au Substrate by Nanoimprint Lithography techniques.

The multidisciplinary field of nanotechnology is bringing the science of the almost incomprehensibly small device closer and closer to reality. The Nanofabrication techniques are classified into bottom-up and top-down methods, where the former is based on chemical reactions giving rise to nanomaterials with compositions, sizes, and shapes determined by the reaction conditions, The ability to fabricate patterns on the micro and nanoscale is very important in micro and nanotechnology for many applications, such as magnetic data storage, optoelectronic devices, and biochip1-nanostructures have attracted considerable attention from the scientific and engineering community over the past decade. Uniform patterns on the micro to nanoscale can be formed using a variety of lithographic techniques. The latter involves the use of lithographic techniques, that is, the synthesis of gold and silver nanostructures. The fabrication of two-dimensional patterns of protein on solid surfaces is an essential technology in the development of a protein chip. Protein chips have potential for greater sensitivity in diagnostic tests and may allowed for the discovery of currently undetectable disease markers. Many patterning techniques, including dip-pen nanolithography and nanocontact printing, have been used to create two dimensional arrays of biomolecules such as DNA.

Applications for Sensing of Cancer-related Biomolecules Using LSPR Sensors

Biomolecules	LSPR particles	Spectral shift	Detection limit
Tumor necrosis factor	Ag nanosphere	29 nm	200 ng/mL
Prostate-specific antigen, (PSA	Au nanodisc	2.2 nm	10^{-8} M
p53 (from head and neck squamous carcinoma)	Triangular Ag nanoparticle	88 nm	59.45 pg/mL
PSA	Au nanosphere	2.75 nm	0.1 pg/mL

6. Fundamentals of LSPR: To explain the fundamentals of LSPR nanobiosensors, we discuss the basic optical properties of precious metal nanoparticles, which are divided into general plasmons in the bulk state, surface Plasmon's, and localized surface plasmons.We also describe the physical theories correlated with LSPR signal generation for scattering phenomenon in spherical and nonspherical nanoparticles and for the relationship between refractive index changes and spectral shifts.

7. Hardware Setup of LSPR: The application of high-sensitivity LSPR in surrounding dielectric environments has advantages for detection at the molecular level. In this section, we discuss the components of LSPR-based nanobiosensor systems for high-sensitivity recognition of biomolecules. First, we describe the dependency of nanoparticles on various conditions, such as size and shape, for detection of high-sensitivity LSPR signals. Then, we have discussed a substrate preparation method that is adsorption and lithographic techniques, and close with LSPR signal detection methods and ways to improve their limits of detection.

8. Conclusion: This paper has highlighted the physical theories and applications of LSPR nanobiosensors. By controlling and tuning the optical behaviors described in the aforementioned physical theories, such as the material, size, shape, and composition of noble metal nanoparticles. *The Optical antennas (OAs) enable the control and manipulation of optical fields at the subwavelength scale.* The sensitivity of LSPR nanobiosensors may be improved. Various approaches with regard to substrate preparation and optical instrumental setup have been presented to illustrate the challenges and suggestions for improvement in detection sensitivity for LSPR sensors. Narrower bandwidth and higher spectral sensitivity are commonly accomplished by lithographic.

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