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Manipulation of Surface Plasmon Resonances for Novel Nanocomposites Matrices

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Abstract- Plasmonic structures are the synthetically prepared metamaterials usually made up of nano-sized noble metals. Such plasmonic materials exhibit unique optical properties different from natural bulk materials. These unique optical properties are due to the excitation of surface plasmons. Strong absorption of light wave is the unique characteristic property of such metamaterials. These have great potential for energy harvesting to sensors applications. The optical performance such as bandwidth, intensity, and peak position of the absorption can be adjusted.
In this work, experiments are performed to develop nanocomposite (NC) metamaterials based coating for light absorption. Metallic gold nanoparticles are incorporated into dielectric matrix (SiO_2 and/or TiO_2) to form ultra-thin NC. In-house PVD-Magnetron sputtering methods are used for NC development.
Experimental results demonstrated that the optical properties can be tuned by varying geometrical structure. It is also found that the dielectric environment has strong influence on the broadening of absorption peak from shorter to longer wavelengths.

Keywords- **:** *Surface plasmons, Surface plasmon resonance (SPR), Metamaterials, Localized surface plasmon resonance (LSPR), Plasmonic superabsorber (PSA), Nanocomposites (NCs), Nanoparticles (NPs).*

I. INTRODUCTION

Plasmonic nanocomposites (NCs) are gaining interest in scientific community due to their extraordinary optical properties for the development of photonic and electronic devices. Super or perfect absorber is one special optical property of metal-dielectric NCs that have attracted lot of attention due to its wide range of applications. These applications include solar power harvesting [1], thermal imaging devices [2] and microbolometer [3]. Because of its wide range of applications, these composites have already been studied in different frequency ranges from microwave, middle-IR (Infrared), and near-IR to visible range [4].

In metal-dielectric NC coating, metallic nanoparticles (NPs) are inserted in dielectric materials with high filling factor (ff). This technique allows us to wide range of applications such as plasmonic superabsorber (PSA) [5]. In visible and near-infrared (NIR) spectra, the surface plasmon resonance (SPR) can be generated at the surface of the metal films when external light is incident [6]. SPR can be obtained by the materials having complex dielectric constant with negative real part and positive imaginary part [5]. Due to the generation of surface plasmons, the localized electromagnetic field around the metal is enhanced around 105 and 1020 times of the incident light for linear and nonlinear optical responses, respectively [7]. This phenomenon happens when electrons get excited and displaced from their position, then the surface charges apply a force for restoration on the displaced electrons resulting in oscillatory motion with a specific frequency called plasmon resonance frequency [8]. Due to this, a field is to be generated inside the particle and dipolar field will occur on the outer surface of particles. The field around the NP can increase their absorption [7]. If the size of metallic NPs is smaller than the wavelength of light "λ", the optical properties of NPs are different from the bulk material [9]. It resulted in exceptional optical properties, such as narrowing of absorption bands which depends not only shape and size of the metallic particles but also on the relative distances between metallic particles [10].
The work presented in this paper is about the experimental studies related to the fabrication and characterization of multi-component PSA for visible and near-infrared wavelength range by magnetron sputtering. Present work is according to the earlier works done in the nanochemistry group [5, 11]. In previous work, PSA was observed by metallic NPs embedded by single dielectric matrix either by SiO_2, where the absorption spectrum was observed at limited frequency ranges. Moreover, in previous work, NC and thick metallic film was separated by insulating spacer layer. Considering these parameters, here we investigated PSA having two dielectric matrices (i.e. SiO_2 and TiO_2). Due to different refractive index

properties of these materials broader absorption could be observed. The NC is in direct contact with metallic film which could increase the more contribution of metallic film and NC and more SPR could be observed. This paper is divided into four sections. Section 1 provides the introduction of the paper. Section 2 reviews the basic literature on NPs, perfect absorbers, SPRs and localized SPRs (LSPRs). Section 3 demonstrates and discusses the results of the paper. In the end, Section 4 concludes the paper.

II. LITERATURE REVIEW

Plasmons and plasmonics are very broad field of pure physics and have gained significant research interest due their wide range of applications [12]. Plasmonic defines how electromagnetic light can be used to manipulate the movement of free electrons in metals. Noble metals such as gold or silver atom has one free electron in their outer most shell just because of that it is known as noble metal and stable. If we talk about number of crystals in gold and silver, we have many free electrons. In the beginning, Roman started to fabricate a glass cup (known as Lycurgus Cup) in 4^{th}century which consist of a very small nanometer sized gold and silver particles [13]. Due to presence of nano-sized noble metallic particles, the LSPRs are excited under the action of visible light. In the Lycurgus cup, the green/yellow color produced when electromagnetic (EM) light is induced from outside and reflected from outer surface, while red color is produced when light is induced inside the cup and transmitted from the inner surface of the cup. This effect for Lycurgus cup was unknown at that time. In the beginning of last century, it was realized that these effects could be attributed to plasmonic resonance. Later, the term "plasmon" for collective oscillations of free electron in the metal under the action of EM light was introduced by Pines [14, 15]. Plasmon is a branch of quantum physics and can be defined by the electron-photon coupling which occur by mechanical vibrations or oscillations of free electrons. This effect of collective oscillations is more pronounced at the interface between metallic NPs and dielectrics. In recent days, plasmonic NCs can be found in many different applications, such as nanometric coatings in emerging fields, such as photonic devices, solar cell and biosensing applications [5].

The fast growth of nanotechnology puts forward higher requirement for nanofabrication techniques. A number of different kinds of techniques have been developed and implemented till now a day for designing nanomaterials with wide range of applications [12]. This is because the properties of material dramatically change when the material thickness changes from bulk to few nanometers. In recent times, metallic nanostructures are the most widely investigated because of their excellent optical properties. When the NPs are placed alongside they have ability to trap stronger field in between as compared to individual NP. This phenomenon is responsible for creating great localized field [16]. Although individual NPs were used as decorative pigments in stained glasses and artworks, but interacting NPs with light provide great localization of electromagnetic field that can be used for variety of applications as compared to bulk [17]. This is due to the charge separation of the NPs excited by LSPs to create dipole mode that follows the polarization of incident light [18]. The resonant mode of the NPs depends on the physical characteristic of the particle. The maximum amplitude of resonance can be obtained at certain frequency of oscillation. This phenomenon is known as SPR which causes strong absorption of light at that resonant frequency. It can be measured using ultraviolet-visible (UV-Vis) absorption spectrometer.

Gold NPs is the one of the best noble metal and has been investigated for several years. Since gold has unique features such as most stability, enhanced and tunable optical properties as well as excellent biocompatibility. Because of these properties, Au NPs can be used in broad range of applications such as in electronic and optical as well as applications in catalysis and biological systems [19]. Not only good stability of gold in the form of NPs but also has an ability to give plasmon resonance (Mie resonance) and good optical properties at visible frequency range [11]. This plasmonic effect is more dominating at surface because the mean free path of gold is around 50 nm and does not encounter bulk scattering. Hence the phenomenon of SPR occurs at surface when light fall on the surface which oscillates the free electrons of noble metals. Not only the geometry of NPs effect on the plasmonic resonance but also the surrounding environment could also effect on the resonance frequency. It is believed that interacting metallic particles with insulating environment could absorb light at wide frequency range [5].

Nowadays, the optical effects associated with nano-sized gold particles are in deep focus of study and are well understood [20]. According to effective medium theory, if the metallic grain size is smaller than the wavelength incident visible light then a wide range of optical properties can be achieved. Particularly metallic gold has been extensively studied. Since metallic Au NPs shows a single absorption peak at 520 nm [21]. It has been shown that the absorption can strongly depend on the diameter of the NPs [22]. The intensity of the SPR can be increased and its wavelength can be shifted by increasing size of the NPs. For larger particles (i.e. more than 100 nm), the higher order modes are dominant that causes the broadening of band [18]. This absorption (A) having no scattering, can be computed from the information of transmittance (T) and reflectance (R) as given by eq (1).

$$A = 1 - T - R \tag{1}$$

A number of different approaches have successfully been achieved for the development of super absorbers. One of them is to develop NC material made up of gold NPs embedded in a dielectric layer. Concerning such type of super absorber achievement, many researchers are now interested to design multi-components super absorber where more than one dielectric material is to be used. In present work, gold NPs were embedded in composite thin film of SiO_2 and TiO_2. This NC was deposited on gold coated glass substrate, in order to achieve better optical properties and stability as compared with classical single dielectric composites. This multi-component NC allows a dramatic change in optical properties such as perfect absorption. TiO_2 is one of the best metallic oxide dielectric used in different applications such as photocatalysis, semiconductor technology and optoelectronic devices. These applications are brought under high consideration becauseTiO2 has a property of chemical stability, high photosensitivity, non-toxicity, low cost, easy availability and environmental friendliness. Beside the TiO_2, SiO_2 as a nano-thin film has also better optical properties. The optical effects of SiO_2 and TiO_2 with noble metal have already been studied (details can be find in the review of plasmonic NC metamaterial [5]). According to this review the broad band perfect absorber in visible frequency has achieved, if the optical glass is to be coated with gold film having 100 nm thickness, 25 nm of SiO_2 and 20 nm of Au SiO_2 NC on the top of the surface.

In present work, super absorption at visible and near-infrared wavelength has been achieved not only by NPs of noble metal embedded single dielectric film but a multicomponent NC was fabricated. This gives us the possibility to further shift the resonance absorption band to NIR. Gold NPs were embedded in composite thin film of SiO_2 and TiO_2. This NC was deposited on gold coated glass substrate.

Super or perfect absorber is one special optical property of metal-dielectric composites which have attracted lot of attention due to its wide range of applications. These applications include solar power harvesting [1], thermal imaging devices [2] and microbolometer [3]. Because of its wide range of applications, these composites have already been studied in different frequency ranges from microwave, middle-IR, near-IR to visible range [4]. In metal-dielectric NC coating, metallic NPs are embedded in a dielectric matrix with high ff. This technique allows us a wide range of applications such as PSA [5].

III. Results and Discussion

In this section, the experimental results of LSPR and SPR are demonstrated. Following previous work [5, 11], a NC has been prepared (i.e. having high and low refractive indices with gold NPs as ff).

The current plasmonic metamaterials performance highly depends on dielectric environment (i.e. SiO_2 and/or TiO_2) of the NC, metallic ff as well as NC film thickness. A number of plasmonic materials are fabricated and investigated by changing film thicknesses, ff and dielectric environment. The percentage of metallic ff and also film thickness were varied from each experiment in order to achieve effective SPRs properties of the current plasmonic metamaterials in visible and NIR frequency range as well.

Gold Film on Glass

Gold as a prime metal is used for present plasmonic material because of its unique optical properties and chemical stability. Fig. 1 shows schematic of the layered structure used in this work. While, Fig. 2 shows real photograph of sample bearing gold coated optical glass. It is a composed of optical transparent glass and 100 nm gold film.

Fig. 1: Schematic of the sample prepared, 100 nm Au deposited on transparent glass.

Fig. 2: Transparent glass (Left), 100 nm Au bare film on glass substrate (Right)

It is known that thick metallic films are excellent mirrors because of their good reflection properties at wide frequency range [9]. The thick metallic film on glass substrate is commonly used to block transmission of light wave. The main objective to use thick film of gold as a base layer in present work is to block the light. Here the base gold film is selected to be as thicker than the skin depth so that the light would not be transmitted through the gold film [16].

A 100 nm Au film on glass substrate (see Fig. 2) was characterized by UV-Vis spectrometry and film thickness was measured by profilometer. As shown in Fig. 3, transmission is almost zero at wide frequency range.

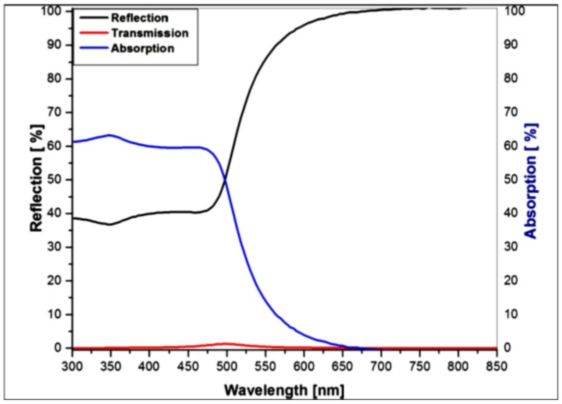

Fig.3:UV-Visabsorption (bluesolidcurve) at 6°, reflection (black solid curve) and transmission (red solidcurve) for 100nm Au on glass substrate

It is shown that the absorption/reflection peak is splitting into two peaks (see Fig. 3). This can be attributed that one of the peak belongs to the LSPRs of nanostructures and the second peak belongs to the SPPs confined at the interface of glass and gold. The SPPs are excited due to the energy transfer from LSPs of the NPs and coupling of gold and glass interface [16]. From Fig. 3, it has been observed that reflection of thick gold film increase at longer wavelength range (i.e. from some part of visible to IR range). On the other hand, the absorption band (around 60%) at shorter wavelengths (from 300nm to 500nm) can also be observed in Fig. 3. This is originated from the band transition from filled "d" band into "sp" conduction band of gold and hence most of metal known as lossy material at shorter wavelengths [17]. It can also be postulated that the resonant frequency of LSPs in gold NPs lies in the visible spectrum of light around 500 nm wavelength which is related to predicated value and strongly dependent on the size shape and distance between metallic NPs. Hence characteristic absorption peak can be seen in between 300 to 500nm in Fig. 3.

Absorption spectra of dielectric matrix with ff

In this section, the optical properties of NC with dielectric matrix (i.e. SiO_2 and TiO_2) on thick metallic film and on glass substrate are presented to observe the resonance shift according to dielectric environment.

Fig.4:Schematic of the sample prepared, NC of Au and SiO_2 deposited on 100 nm gold film.

The top layer plasmonics NC consists of metallic ff (i.e. Au NPs) surrounded by dielectric environment as shown in Fig.4 and Fig.5 respectively.

Fig. 5: Schematic of the sample prepared, NC of Au and TiO_2 deposited on 100 nm gold film.

One can observe from Fig. 6, the absorption peak (blue peak) is high at shorter wavelength of pure SiO_2 matrix and going to be decreased at longer wavelength range. This shift of the absorption band to shorter wavelength is because of the low dielectric constant and index of refraction of SiO_2 on the resonance of metallic particles is more dominant in visible range. While in contrast with pure SiO_2 matrix peak, the absorption peak (red peak) is high at NIR range for pure TiO_2 matrix (see Fig. 6). This longer wavelength peak is because of higher dielectric constant of TiO_2 as the resonance of metallic particles is more dominant at NIR range.

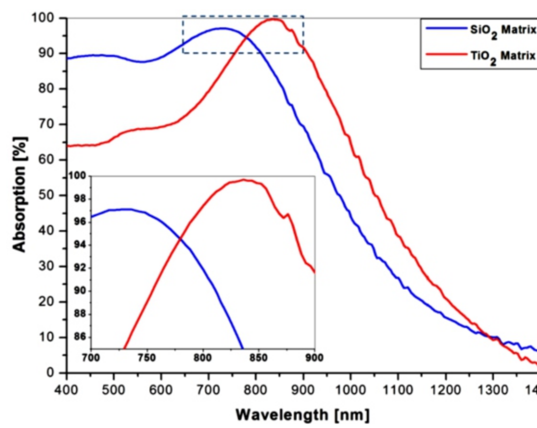

Fig.6:UV-Vis absorption spectra at 6° for NC with pure SiO_2 matrix (blue curve), pure TiO_2 matrix (red curve) on thick metallic gold film (100 nm Au film). The ff of gold and NC film thickness are kept constant i.e. 40% and 50 nm, respectively. Magnified plot is shown in inset.

The reflection and transmission spectra of 50 nm NC with constant gold NPs (40% ff) surrounded by SiO_2 and pure TiO_2 matrix on glass substrate (without mirror (Au) film) are presented in Fig. 7 and Fig. 8, respectively, in order to investigate the effect of dielectric matrix on NC without thick mirror film.

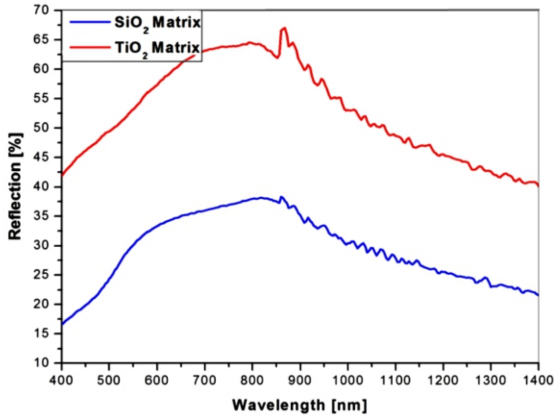

Fig. 7: UV-Vis reflection spectra at 6° for NC with pure SiO_2 matrix (blue curve), pure TiO_2 matrix (red curve) on thick gold film (100 nm Au film). The ff of gold and NC film thickness are kept constant i.e. 40% and 50 nm, respectively.

From Fig. 7 and Fig. 8, one can see that the reflection intensity of pure TiO_2 matrix is higher as compared to reflection intensity of pure SiO_2 matrix, while (as opposed to reflection) the transmission intensity of pure TiO_2 matrix is lower as compared to transmission intensity of pure SiO_2 matrix. If we measure the absorption intensity (as given by eq (1) for both pure SiO_2 and TiO_2 matrix, we will see that the absorption intensity is high in visible range for pure SiO_2 matrix while for pure TiO_2 the absorption is higher at NIR range. As explained already that the dielectric matrix in terms of index of refraction is playing major role for peak shifting. Not only dielectric matrix plays a major role for peak shifting but also the other constant parameter (i.e. ff and film thickness) may also influence on resonance shift.

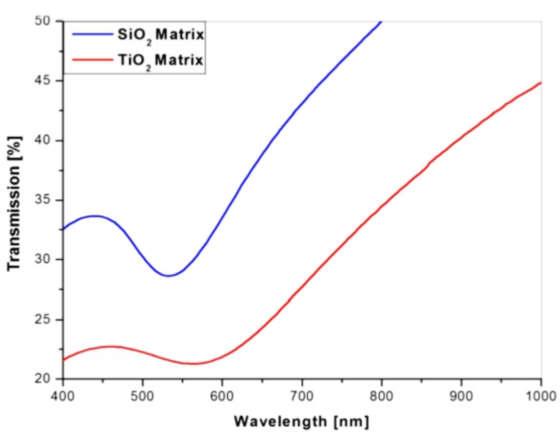

Fig. 8: UV-Vis transmission spectra at 6° for NC with pure SiO_2 matrix (blue curve) and pure TiO_2 matrix (red curve) on thick gold film (100 nm Au film). The ff of gold and NC film thickness are kept constant i.e. 40% and 50 nm, respectively.

IV. Conclusion

The effective optical properties and plasmonic behavior of NC for visible and near-infrared frequency range are observed. This NC (out of three materials, two dielectrics and one metal) is deposited on optically thick gold film. The NC and base film are then characterized by UV-Vis spectrometer and ellipsometer to investigate the effective optical properties. In this work two types of SPRs i.e. LSPRs and SPRs have been studied for novel NCs. Experimental results illustrated that the effect of dielectric environments in resonance peak shifting.
The proposed PSA can be used in the applications of nano-coatings, sensing, and the development of photovoltaic solar panels. The simple, straightforward and cost-effective concept is reported in this work. As an outlook, theoretical analysis is required for studying real mechanism behind experimental observations. It may further involve the theoretical modeling of resonant modes excited in PSA.

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