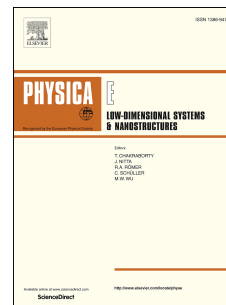


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Graphene vs. Silica Coated Refractory Nitrides based Core-Shell Nanoparticles for Nanoplasmonic Sensing

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Abstract

Plasmonic nanoparticles based on conventional metals like gold (Au) and silver (Ag) has attracted significant attention of biosensor researchers. Core-shell nanoparticles (CSNP) have shown specific advantages by virtue of unique combination of strong field enhancement and wide ranging spectral tuneability of localized surface plasmon resonances (LSPR). In view of the remarkable plasmonic properties of refractory nitrides (*e.g.*, ZrN and TiN) like higher degree of spectral tuneability, growth compatibility, high melting point, inherent CMOS and biocompatibility etc., and reported high surface area, excellent bio-molecular compatibility, improvement in the speed, higher sensitivity in graphene, the present work assess the feasibility of graphene coated refractory nitrides based CSNP as an efficient refractive index sensor. Mie theory is employed for the theoretical analysis and simulation of such plasmonic structures. The results reported in the present work have been corroborated using COMSOL. The comparison of plasmonic properties and sensing characteristics *e.g.*, FWHM, quality factor, sensitivity and figure of merit is presented for graphene and silica based sensors. It is reported that the sensitivity=171.68 (nm/RIU) and figure of merit= 3.57×10^4 (nm/RIU) can be attained. The present work suggests that graphene coated refractory nitrides based core-shell structures may emerge as ultrasensitive biosensor.

Keywords: core-shell, nanoparticle, plasmonic sensor, biosensor, Mie scattering theory, refractory nitride, graphene

1. Introduction

In the backdrop of the fast growing world population, the need of developing efficient healthcare systems and devices is at its peak [1-2]. In turn, it is therefore mandatory to explore the possibility and scope for developing efficient, long lasting, economical and practically feasible solutions to the existing as well as future medical challenges posing threat to the existence of humanity like the pandemic spread of COVID-19. Plasmonic systems and devices exploiting unique features of hybrid quanta known as surface plasmons are emerging as the backbone of medical diagnostics *e.g.*, large efforts of physicists, chemists, biologists, material scientists *etc.* are focused on the development of ultrasensitive plasmonic detectors for biosensing applications [3, 4]. For the sake of completeness, this is to be emphasized that the plasmonic systems based on both, the propagating surface plasmons as well as localized surface plasmons are being investigated and considered for their applications in optoelectronic integration, light harvesting, energy transfer, cancer therapy, food safety, environmental monitoring, surface enhanced Raman spectroscopy (SERS) *etc.* [5-13]. As far as localized surface plasmon resonance (LSPR) based sensing is considered, gold (Au) has been the most widely used conventional plasmonic material for theoretical exploration and experimental investigations. Since long, the plasmonics has been suffering from the limited number of plasmonic materials, resulting in the underutilized potential of plasmonics. In order to expand the domain of plasmonics, it is obligatory to expand the list of plasmonic materials beyond conventional plasmonic materials *e.g.*, gold, silver, copper *etc.* Refractory nitrides such as TiN and ZrN has recently been explored for their applications in biosensing [5]. Moreover, graphene coated nanoparticles have also emerged as effective plasmonic systems based on alternative plasmonic materials [14]. Due to their exceptional optical, electrical, thermal and mechanical properties, graphene and its derivatives are considered to be the promising materials for biosensing [15-16]. In order to improve the performance of nanoparticle based plasmonic sensors, it is required that the scattering efficiency increase and the line-width or full width half maximum (FWHM) of plasmonic resonances decrease. As reported in Ref. [5], this was attained using plasmonic nanoparticle structures and optical gain incorporation in the dielectric layer. Although the gain incorporation is a viable alternative, this will lead to the enhanced complexity and the cost of the sensor. Therefore, it will be of great use if one can enhance the sensor performance without optical gain incorporation. There are different ways to secure reduce full width at half maximum. The use of Fanomodes closely packed

nanodisk clusters are among such approaches [17]. Obviously, the sensitivity and other sensing characteristics also depend on the choice of material, size, shape and the nature of embedding medium. The graphene layer can be combined with the conventional plasmonic nanostructures to improve the interaction between the graphene and the incident electromagnetic radiation. These reports and literature survey suggests that the use of graphene coated nanoparticles are extremely advantageous for sensing applications [18, 19]. Graphene can also be placed in different kinds of optical microcavities [20]. Also, the patterned periodic graphene islands improve the plasmonic interactions and effects significantly [21]. Since the successful isolation and first characterization of graphene in 2004, there has been the quest to explore the applications of graphene in energy harvesting, display panels, solar cells, sensing etc. [22-29]. Graphene shows fairly good plasmonic response MIR and FIR spectral region. A large volume of efforts are focused on increasing the light absorption using graphene. For example, it has been shown that the light absorption can be enhanced by placing a graphene layer in nano-cavities. By integrating the graphene with metal gratings, and photonic crystal cavity, enhancement $\sim 70\%$, and 85% , respectively has been reported [30, 31]. Increasing the graphene absorption normally results in narrower absorption peaks and thus higher figure of merit of the sensor. In Ref. [32], graphene is used as a spacer between the Au film and Au nanoparticles to obtain larger FOM relative to that one without graphene spacer. Furthermore, the size and geometry of the nanoparticle are another two main parameters that affect the sensitivity and the FOM of a LSPR sensor [7-14]. There are many reported LSPR sensors with different nanoparticle shapes *e.g.*, spherical [33-34], nanocube [22], nanoprism, nanopyramid [34], nanoring [35], and nanobelt [36]. Recently, [38] proposed a temperature sensor using ternary structure in which one of the layers is superconducting material where the sensitivity of 31.18 nm/K has been reported. Photonic crystals have also been used for sensing devices in biomedical applications. Ramanujam *et.al.* proposed RI sensor for cancer and, 43 nm/RIU sensitivity was reported [38]. In view of the remarkable plasmonic properties of refractory nitrides (*e.g.*, ZrN and TiN) like higher degree of spectral tuneability, growth compatibility, high melting point, inherent CMOS and biocompatibility etc. [5], and reported high surface area, excellent bio-molecular compatibility, improvement in the speed, higher sensitivity in graphene, the present work assess the feasibility of graphene coated refractory nitrides based CSNP as an efficient refractive index sensor. Mie theory is employed for the theoretical analysis and simulation of such plasmonic structures. The results reported in the

present work have been corroborated using COMSOL. The comparison of plasmonic properties and sensing characteristics *e.g.*, FWHM, quality factor, sensitivity and figure of merit is presented for graphene and silica based sensors. Specially, the case of sensing blood with different plasma concentrations is taken as an example for demonstration.

The objective of the present article is to: **(I)**. estimate the sensing characteristics of ZrN (core)-graphene (shell) and TiN (core)-graphene (shell) structure, **(II)**. estimate the sensing characteristics of ZrN (core)-silica (shell) and TiN (core)-silica (shell) structure, **(III)**. compare sensing characteristics of graphene assisted structure with silica assisted structure, **(IV)**. investigate the role of aspect ratio (r_1/r_2) on sensing characteristics, **(V)**. establish the dependence of sensing characteristics on aspect ratio through fitting equations, perceived to be of key importance for developing appropriate designs, **(VI)**. propose different design strategies for obtaining improved sensor performance.

The manuscript is organized as follows. Section II describes the theoretical description, giving simple details of the theory. Section-III presents the results of our investigations. The concluding remarks are given in Sec. IV.

2. Theoretical Description

The schematic diagram of representative core-shell nanoparticle (CSNP) based plasmonic sensor is shown in Fig. 1. The structure consists of transition metal nitride (*e.g.*, TiN, ZrN) core (permittivity ϵ_1 and radius r_1), and graphene or SiO₂ shell (permittivity ϵ_2 , radius r_2 and thickness d). The core-shell system is surrounded by the sensing medium (dielectric constant, ϵ_3 and refractive index, n). The optical properties of this system are investigated using Mie scattering theory, which is an effective analytical tool for theoretical analysis of spherical, core-shell, cylindrical nanoparticles etc. [3, 33, 39]. Besides these particle shapes, Mie scattering theory is extendible to multilayered core-shell nanoparticles (MCSNP) also [39]. For core-shell nanoparticle system considered in the present work, Mie theory expression for scattering efficiency (Q_{sca}) is expressed in the following form [5, 33]:

$$Q_{sca} = \frac{2}{x^2} \sum_{n=1}^{\infty} [2n+1] (|a_n|^2 + |b_n|^2) \quad (1)$$

where, x is the size parameter and the coefficients for scattered fields a_n and b_n are defined as [5],

$$a_n = \frac{\psi_n(x_2)[\psi'_n(m_2x_2) - A_n\xi'_n(m_2x_2)] - m_2\psi'_n(x_2)[\psi_n(m_2x_2) - A_n\xi_n(m_2x_2)]}{\xi_n(x_2)[\psi'_n(m_2x_2) - A_n\xi'_n(m_2x_2)] - m_2\xi'_n(x_2)[\psi_n(m_2x_2) - A_n\xi_n(m_2x_2)]} \quad (2)$$

$$b_n = \frac{m_2\psi_n(x_2)[\psi'_n(m_2x_2) - B_n\xi'_n(m_2x_2)] - \psi'_n(x_2)[\psi_n(m_2x_2) - B_n\xi_n(m_2x_2)]}{m_2\xi_n(x_2)[\psi'_n(m_2x_2) - B_n\xi'_n(m_2x_2)] - \xi'_n(x_2)[\psi_n(m_2x_2) - B_n\xi_n(m_2x_2)]} \quad (3)$$

also,

$$A_n = \frac{m_2\psi'_n(m_1x_1)\psi_n(m_2x_1) - m_1\psi_n(m_1x_1)\psi'_n(m_2x_1)}{m_2\psi'_n(m_1x_1)\xi_n(m_2x_1) - m_1\psi_n(m_1x_1)\xi'_n(m_2x_1)} \quad (4)$$

$$B_n = \frac{m_2\psi_n(m_1x_1)\psi'_n(m_2x_1) - m_1\psi'_n(m_2x_1)\psi_n(m_1x_1)}{m_2\psi_n(m_1x_1)\xi'_n(m_2x_1) - m_1\psi'_n(m_1x_1)\xi_n(m_2x_1)} \quad (5)$$

where, m_1 and m_2 are the refractive indices of core and the shell relative to the surrounding medium. Also, $x_1 = kr_1$ and $x_2 = kr_2$ are size parameter and, $\psi_n(x) = xj_n(x)$ is the Riccati-Bessel function of first kind and, $\xi_n(x) = xh_n^{(2)}(x)$ denotes the Hankel function of second kind. For the nanoparticle under consideration, Q_{scd} is calculated using Eq. 1. The approach used here is versatile as it can be used for the variety of nanoparticle systems and can be easily extended to different spectral regions and also to different material systems.

2. Results and Discussion

In this section, results of our investigations concerning design considerations for graphene/SiO₂coated ZrN/TiN based plasmonic structure as shown in Fig. 1 are presented. The thickness dependent optical response of graphene is considered using Kubo's formula[27, 30]. The conductivity (σ) of an infinitesimal thin graphene sheet depends on the frequency of interacting light, and the surface conductivity is the sum of intra-conductivity (σ_{intra}) and inter-conductivity (σ_{inter}), described as follows [39, 40]:

$$\sigma_{intra} = \frac{ie^2k_BT}{\pi\hbar(\omega + i/\tau)} \left(\frac{\mu_c}{k_BT} + 2 \ln(e^{\frac{\mu_c}{k_BT}} + 1) \right) \quad (6)$$

$$\sigma_{inter} = \frac{ie^2}{4\pi\hbar} \ln \left(\frac{2\mu_c - (\omega + i/\tau)\hbar}{2\mu_c + (\omega + i/\tau)\hbar} \right) \quad (7)$$

Here, ω is the frequency of incident radiation, μ_c is the chemical potential [31], τ is the relaxation time ($\tau^{-1} \leq 1.0$ meV), T is the temperature, and $\hbar$ is the reduced Planck's constant. The thickness (d) dependent relative permittivity of graphene is expressed as [42],

$$\epsilon_{gr} = 1 + i\sigma/(\epsilon_0\omega d) \quad (8)$$

Figure 2 shows the variation of real and imaginary parts of the refractive index of graphene as a function of chemical potential (μ_c) for graphene thickness = 0.34 nm. The calculations are performed at a fixed wavelength, $\lambda = 1550$ -nm and constant temperature, T . The validity of calculated (solid line) graphene data is corroborated by its comparison with the data reported in Ref. 40 (open circles). It is clearly visible that, the real and imaginary parts of graphene refractive index crosses each other at $\mu_c = 0.5$ eV, which is referred to as the epsilon-near-zero (ENZ) point. Epsilon-near-zero point refers to the point above which graphene shows metallic behavior. The high confinement of optical plasmonic modes to the graphene ensures high light-matter interaction that enhances nonlinear optical processes [41]. The calculated data (solid line) shows an excellent agreement with that reported in Ref. 40 (open circles). The spectral variation of real (ϵ_g') and imaginary (ϵ_g'') parts of the dielectric function of graphene for different chemical potential values ($\mu_c = 0.46, 0.48$ and 0.50 eV) is presented in Fig. 3 (a, and b), respectively (solid lines). Also shown is the corresponding data (open circles) from Ref. [42]. The excellent agreement between present data and that from literature validates the use of present data for further analysis. The spectral variation of the real and imaginary part of graphene for different graphene thicknesses ($d_g = 1.0$ and 1.2 nm) is shown in Fig. 4. Also shown is the variation of corresponding real and imaginary part of the refractive index. For the sake of enhanced clarity and readability, the data in wavelength as well as energy terms is plotted. The calculations are performed at chemical potential, $\mu_c = 1.0$ eV and temperature, $T = 300$ K.

The Mie scattering theory calculated (solid lines) spectral variation of scattering efficiency of optimized CSNP (30, 32.5) for TiN/ZrN core and graphene shell is presented in Fig. 5. The shell here is taken as the graphene layer of thickness 2.5 nm. For the sake of validation of these calculations, Mie theory results (solid line) have also been compared with the results obtained from FEM solver COMSOL (open circle). An excellent agreement between Mie theory and COMSOL calculations is evident. The system is considered to be embedded in the medium of refractive index, $n = 1.417$. It is evident that the scattering spectra shows resonance peaks at,

$\lambda_R=1165.38$ and 1162.96 -nm for ZrN, and TiN cores, respectively. This is evident that the resonance peak lies in the near infrared region for the system under consideration. The excellent agreement with COMSOL suggests the validity of our MATLAB code.

The calculated maps (using COMSOL) in Y-Z plane for the norm of the electric field normalized to the incoming electric field, $|E_{tot}/E_{inc}|$ for TiN-Graphene, and ZrN-Graphene core-shell nanoparticle (CSNP) are shown in **Fig. 6**. For these calculations, $r_1=30$ nm and $r_2=32.5$ nm and the CSNP is labeled as CSNP (30, 32.5), where the first and the second index refers to the core and shell radius (nm), respectively. The calculations are performed at the peak wavelengths, which are 1166.0 nm and 1163.2 nm for TiN and ZrN, respectively. The calculated spectral variation of scattering efficiency for SiO₂/graphene coated core-shell nanoparticle, CSNP (30, 32.5) consisting of TiN and ZrN core is shown in Fig. 7(a-b) (solid lines). The particle is considered to be surrounded by the medium of refractive index, $n=1.339$. This is found that the resonance peaks in scattering efficiency spectra can be fitted into the Lorentzian expression,

$Q = Q_0 + \left(\frac{2A}{\pi} \right) \frac{w}{4(\lambda - \lambda_R)^2 + w^2}$, where Q_0 , A , w , and λ_R , represents the baseline shift, the area under the curve, FWHM, and resonance wavelength, respectively. The data fitted into the Lorentzian distribution is also shown (open circles). The values of w (nm) and λ_R (nm) obtained from fitting are (100.46, 642.99), (46.78, 537.63), (8.55, 1152.13), and (5.32, 1150.17) for TiN/SiO₂, ZrN/SiO₂, TiN/Graphene, and ZrN/Graphene, respectively. The comparison of sensing characteristics *e.g.*, peak scattering efficiency (Q_{sca}), peak wavelength (λ_R), FWHM, sensitivity (S), quality factor (QF) and figure of merit (FOM) for TiN-SiO₂, TiN-Graphene, ZrN-SiO₂, and ZrN-GrapheneCSNP (30, 32.5) is summarized in **Table-1**. The system is considered to be embedded in the defected blood having different plasma concentrations. **Table-2** shows the comparison of performance parameters between similar recent research and the present work.

Next, consider a practical example, where sensing medium is the defected blood containing different concentrations of plasma. The dependence of refractive index of blood with plasma concentration C_p is described by the following expression [38],

$$n = 1.32459 + 0.001942C_p \quad (9)$$

where, 1.32459 corresponds to the refractive index of blood with $C_p=0$ and C_p is the plasma concentration in blood and it is measured in the units of g/l. In present calculations, C_p varies from 0 g/l to 50 g/l in the steps of 10 g/l and its corresponding refractive index (n) is

calculated. The variation of resonance wavelength (λ_R) with the refractive index (n) of the defected plasma in blood compound (surrounding medium), $n = 1.339, 1.359, 1.378, 1.397, 1.417$, is shown in **Fig. 8** for, (a). TiN/SiO₂, ZrN/SiO₂, and (b). TiN/Graphene, ZrN/Graphene with SiO₂/Graphene based CSNP (30, 32.5) with SiO₂/Graphene thickness = 2.5 nm. The calculations are performed at five different blood plasma concentrations, 10 g/l, 20 g/l, 30 g/l, 40 g/l and 50 g/l. Other parameters are: $r_1 = 30$ nm, $r_2 = 32.5$ nm, and $\mu = 1.0$ eV. This is evident that the peak wavelength varies as straight line with the refractive index of the surrounding medium. However, the slope of these straight lines is visibly different. The slope of these variations is the measurement of sensitivity of these sensors. These refractive index values, for example, may represent different plasma concentration of defected plasma in blood. The results suggest that λ_R is a very sensitive function of the refractive index of surrounding medium. Next, we focus on estimating the sensitivity (S), which is defined as the rate of change of the peak wavelength with the refractive index, and the same is mathematically written as, $S = d\lambda/dn$. The quality factor of plasmonic resonance is defined as, $QF = \frac{\lambda_R}{FWHM}$, where λ_R denotes the resonance wavelength in the scattering efficiency spectra. The sensor figure of merit (FOM) is defined as the product of sensitivity (S) and the quality factor (QF), viz. $FOM = S \times QF$. The effect of aspect ratio (r_1/r_2) on resonance wavelength (λ_R), quality factor (QF), sensitivity (S) and figure of merit (FOM) for TiN/SiO₂ and ZrN/SiO₂ core-shell nanoparticles are shown in **Fig. 9** (a-d). All these variations are also fitted (into polynomial) and the fitted data is shown through circles. Similarly, the effect of aspect ratio (r_1/r_2) on resonance wavelength (λ_R), quality factor (QF), sensitivity (S) and figure of merit (FOM) for TiN/Graphene and ZrN/Graphene core-shell nanoparticle is shown in **Fig. 9** (e-h). All these variations are also fitted and the fitted data is shown as circles. Unless mentioned otherwise, $\mu_c = 1.0$ eV, and $T = 300$ -K for all calculations. This is observed that λ_R vs. aspect ratio (r_1/r_2) follow straight line for SiO₂ as well as graphene shell. The variation of QF with aspect ratio follows straight line (first order polynomial) for SiO₂ shell while for graphene, the variation is quadratic (second order polynomial). Also, in case of SiO₂ shell, the QF decrease with aspect ratio, while for graphene shell, QF increase with aspect ratio. Interestingly, it can be seen that the variation of S with aspect ratio is quadratic for both, SiO₂ as well as graphene shell. However, the dependence in two cases is opposite. In SiO₂ shell, S increase with aspect ratio and decrease with aspect ratio for graphene shell. Similar variation can be seen for FOM also. It is observed

that the graphene assisted core-shell nanoparticle structure produces higher sensitivity (S) and figure of merit (FOM). Also it is evident that ZrN core produces higher sensitivity in case of SiO₂ shell and it is nearly equal in case of graphene shell. Moreover, higher FOM is obtained for ZrN core compared to TiN shell. The fitting parameters for TiN/SiO₂, ZrN/SiO₂, TiN/Graphene and ZrN/Graphene core-shell nanoparticles. These are fitted into the polynomial, $y = a_0 + a_1(r_1/r_2) + a_2(r_1/r_2)^2$, where y represents λ_R , QF, S and FOM. In summary, ZrN core shows clear advantage compared to TiN core for SiO₂ shell. Graphene assisted CSNP shows clear edge over dielectric shell such as SiO₂. The analysis suggests that compared to dielectric shell, better sensing characteristics can be obtained for graphene coated structure. The following conclusions can be drawn: (I). resonance wavelength can be fine tuned by controlling aspect ratio, (II). aspect ratio can be optimized to obtain best sensitivity or FOM, (III). graphene coated CSNP produces higher sensitivity and FOM compared to that of dielectric coated CSNP, (IV). ZrN exhibit sensing characteristics superior than that of TiN, (V). sensing characteristics are more sensitive to the graphene thickness compared to the case of dielectric.

4. Conclusions

In conclusion, TiN-SiO₂, ZrN-SiO₂, TiN-Graphene and ZrN-Graphene-based core-shell nanoparticle systems are assessed for their suitability as plasmonic sensors. The analysis suggests that, (I). resonance wavelength can be fine tuned by controlling aspect ratio, (II). aspect ratio can be optimized to obtain best sensitivity or FOM, (III). graphene coated CSNP produces higher sensitivity and FOM compared to that of dielectric coated CSNP, (IV). ZrN exhibit sensing characteristics superior than that of TiN, (V). sensing characteristics are more sensitive to the graphene thickness compared to the case of dielectric. Moreover, refractory nitrides like TiN, and ZrN can serve as alternative plasmonic materials. The sensitivity of graphene assisted sensors can be significantly enhanced without gain incorporation and hence maintaining the simplicity of the system.

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Data Availability Statement

All data generated or analysed during this study are included in this published article.

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Table 1: The comparison of sensing performance parameters for CSNP (30, 32.5) (based on TiN and ZrN). The system is considered to be embedded in the defected blood having 10 g/l plasma concentration.

Core-Shell nanoparticle, $r_1=30$ nm and $r_2=32.5$ nm, $\epsilon_3= 1.339$				
Material	TiN-SiO₂	TiN-Graphene	ZrN-SiO₂	ZrN-Graphene
$\lambda_R(\text{nm})$	642.99	1152.13	537.63	1150.17
Q_{sca}	0.50	11.52	4.30	27.92
FWHM(nm)	100.46	8.55	46.78	5.32
S(nm/RIU)	108.64	171.68	137.26	165.40
QF	6.40	134.74	11.49	215.95
FOM (nm/RIU)	6.9×10^2	2.31×10^4	1.57×10^3	3.57×10^4

Table 2: Comparison of the sensitivity between similar recent works and this work.

Sr. No.	References	Sensitivity (nm/RIU)
1	H. Y. Lin, C. H. Huang, G. L. Cheng et. al. [46]	51.0
2	H. J. El-Khozondar, P. Mahalakshmi, R. J. El-Khozondar et.al. [40]	51.5
3	Y. Wang, F. Q. Pu, Y. J. Gu, P. Xu et.al. [47]	71.0
4	P. Pathania, and M. S. Shishodia [39]	77.9
5	In This Work	171.6

Table 3: Fitting parameters for TiN/SiO₂, ZrN/SiO₂, TiN/Graphene and ZrN/Graphene core-shell nanoparticles. These are fitted into the polynomial, $y = a_0 + a_1x + a_2x^2$.

		TiN-SiO ₂	ZrN-SiO ₂	TiN- Graphene	ZrN- Graphene
λ_R (nm)	a_0	8.2E2	-2.1E2	6.4E3	6.4E3
	a_1	-1.9E2	7.3E2	-5.7E3	-5.7E3
QF	a_0	8.22	8.15	8.4E4	10.6E4
	a_1	-1.95	3.74	-1.8E5	-2.2E5
	a_2	-	-	9.6E4	1.2E5
S (nm/RIU)	a_0	-1.2E2	-1.5E2	1.6E4	1.7E4
	a_1	3.8E2	5.2E2	-3.2E4	-3.4E4
	a_2	-1.4E2	-2.2E4	1.5E4	1.6E4
FOM (nm/RIU)	a_0	-9.0E2	-1.9E3	1.2E6	1.9E6
	a_1	3E3	6.2E3	-2.2E6	-3.4E6
	a_2	-1.3E3	-2.5E3	1.0E6	1.5E6

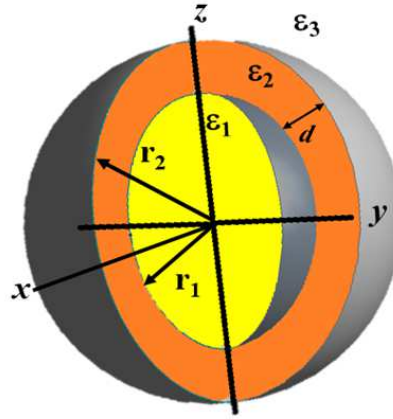


Fig. 1: The schematic diagram of representative core-shell nanoparticle (CSNP) based plasmonic sensor. The structure consists of transition metal nitride (*e.g.*, TiN, ZrN) core (permittivity ϵ_1 and radius r_1), and graphene or SiO₂ shell (permittivity ϵ_2 , radius r_2 and thickness d). The core-shell nanoparticle system is surrounded by the sensing medium (dielectric constant, ϵ_3 and refractive index, n).

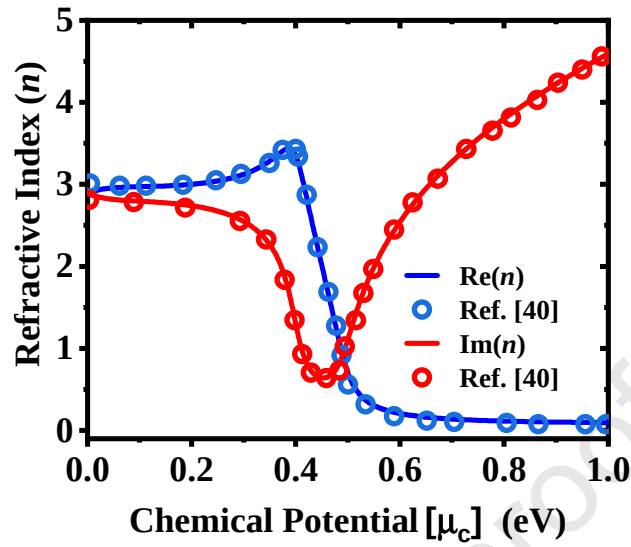


Fig. 2: The variation of real $\{\text{Re}(n)\}$ and imaginary $\{\text{Im}(n)\}$ parts (solid line) of the refractive index of graphene as a function of chemical potential (μ_c). Evidently, the calculated data (solid line) shows an excellent agreement with that reported in Ref. 40. Other parameters are: $d=0.34$ -nm, $T=300$ -K.

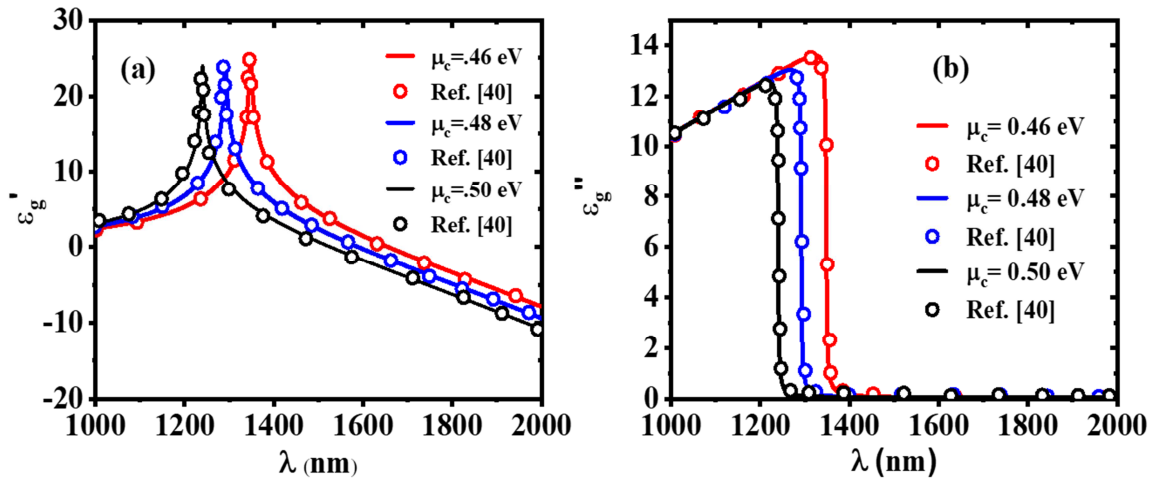


Fig. 3: The spectral variation of real (a), and imaginary (b) parts of the dielectric function of graphene for three different chemical potential values namely, $\mu_c=0.46$, 0.48 , and 0.50 eV. The thickness of graphene layer is 0.34 nm. The calculated data (solid line) is compared with that reported in Ref. [42]. The excellent agreement between two data sets validates the use of present data for subsequent analysis.

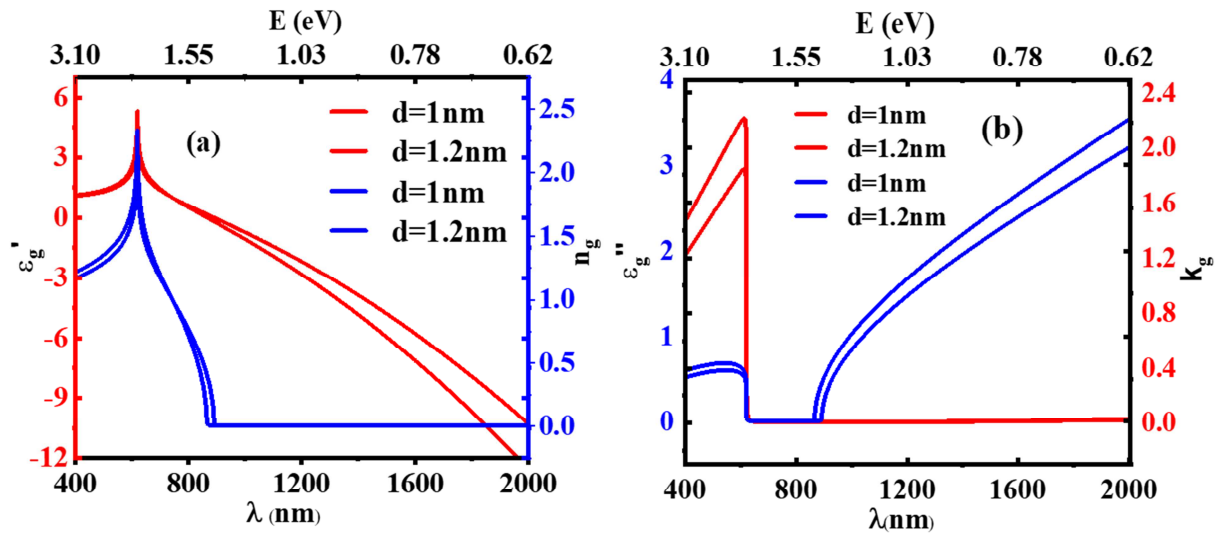


Fig. 4: The spectral variation of real (a), and imaginary (b) parts of dielectric function and complex refractive indices at $\mu_c = 1.0$ eV, for different graphene thicknesses ($d_G = 1.0$ and 1.2 nm). For the sake of enhanced clarity and readability, the data in wavelength as well as energy terms is plotted. Other parameters are: $T = 300$ -K.

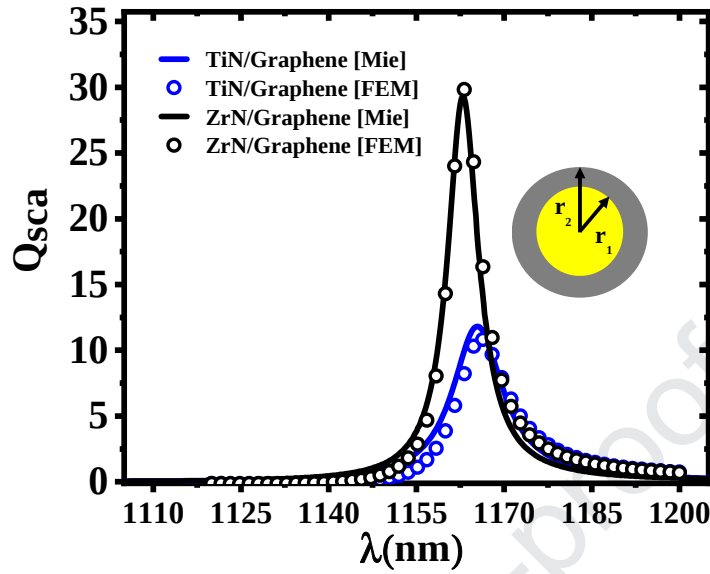


Fig. 5: The calculated scattering efficiency of CSNP (30, 32.5) using Mie scattering theory. The shell is taken as the graphene layer of thickness 2.5 nm. For the sake of validation of our calculations, Mie theory results (solid line) have been compared with the results obtained from FEM solver COMSOL (open circle). An excellent agreement between Mie theory and COMSOL calculations is evident. The system is embedded in the medium of refractive index, $n=1.417$. Here $\mu_c = 1.0$ eV and $T=300$ K.

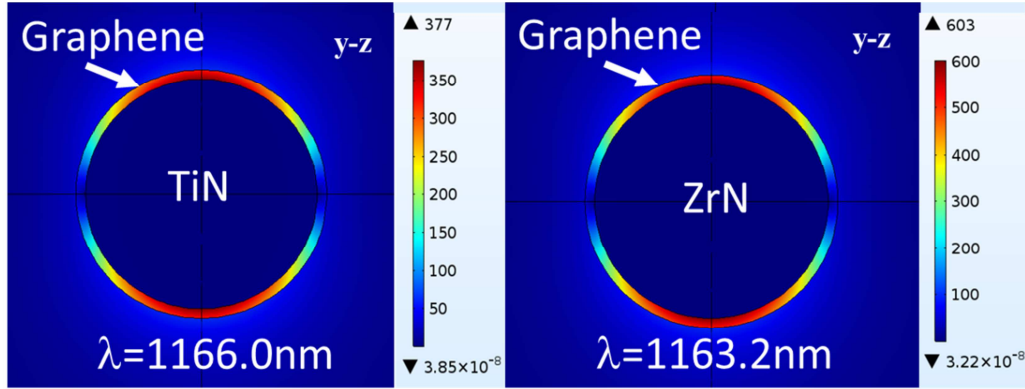


Fig. 6: The calculated maps in Y-Z plane for the norm of the electric field normalized to the incoming electric field, $|E_{\text{tot}}/E_{\text{inc}}|$ for TiN-Graphene, and ZrN-Graphene core-shell nanoparticle (CSNP). For these calculations, $r_1=30 \text{ nm}$ and $r_2=32.5 \text{ nm}$ and the CSNP is labeled as CSNP (30, 32.5), where the first and the second index refers to the core and shell radius (in nm), respectively. The calculations are performed at the peak wavelengths, which are 1166.0 nm and 1163.2nm for TiN and ZrN, respectively at $\mu_c = 1 \text{ eV}$. Other parameters are same as in Fig. 5.

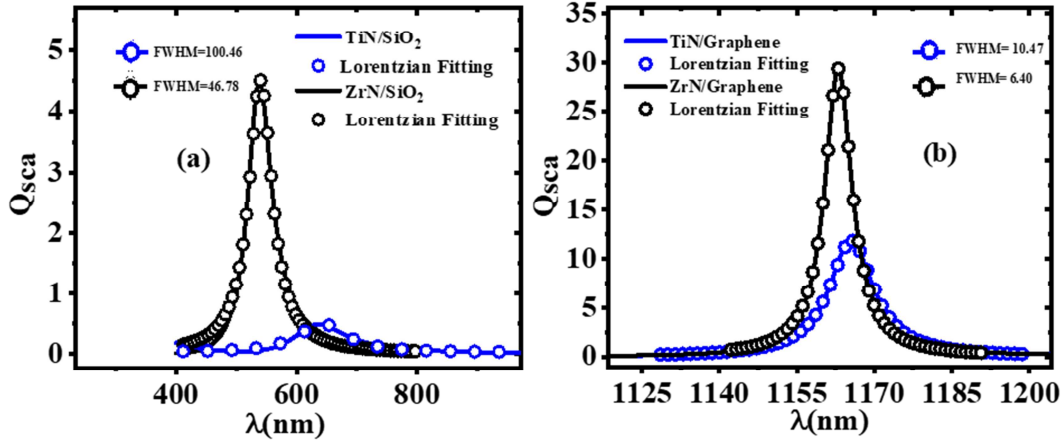


Fig. 7: Lorentzian fitting for resonance peaks for (a). TiN-SiO₂ and ZrN-SiO₂ with SiO₂ thickness, $d=2.5$ -nm, (b). TiN-Graphene and ZrN-Graphene with graphene thickness, $d=2.5$ -nm. Also shown is the FWHM for the surrounding medium with the refractive index of defected plasma in blood compound as surrounding medium is 1.339. Here, core-shell nanoparticle dimensions are (30, 32.5) at $\mu_c = 1.0$ eV.

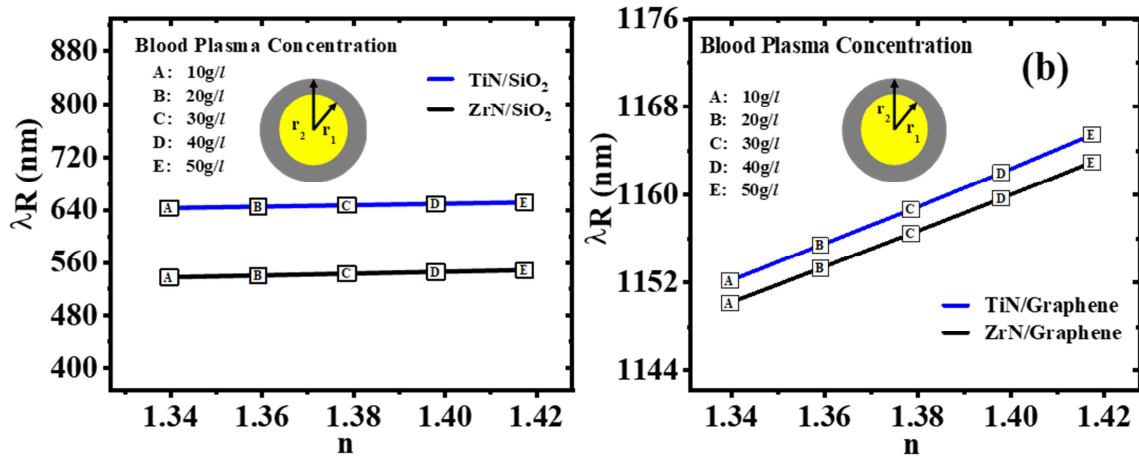


Fig. 8: Calculated dependence of the resonant wavelength (λ_R) on the refractive index (n) of the surrounding medium for (a). TiN-SiO₂ and ZrN-SiO₂ with SiO₂ thickness, $d_{\text{SiO}_2}=2.5$ nm, and (b). TiN-Graphene and ZrN-Graphene with graphene thickness $d_G=2.5$ nm. The calculations are done at five different blood plasma concentrations, 10g/l, 20g/l, 30g/l, 40g/l and 50g/l. Other parameters are: $r_1=30$ nm, $r_2=32.5$ nm. The sensitivity is simply the slope of these lines.

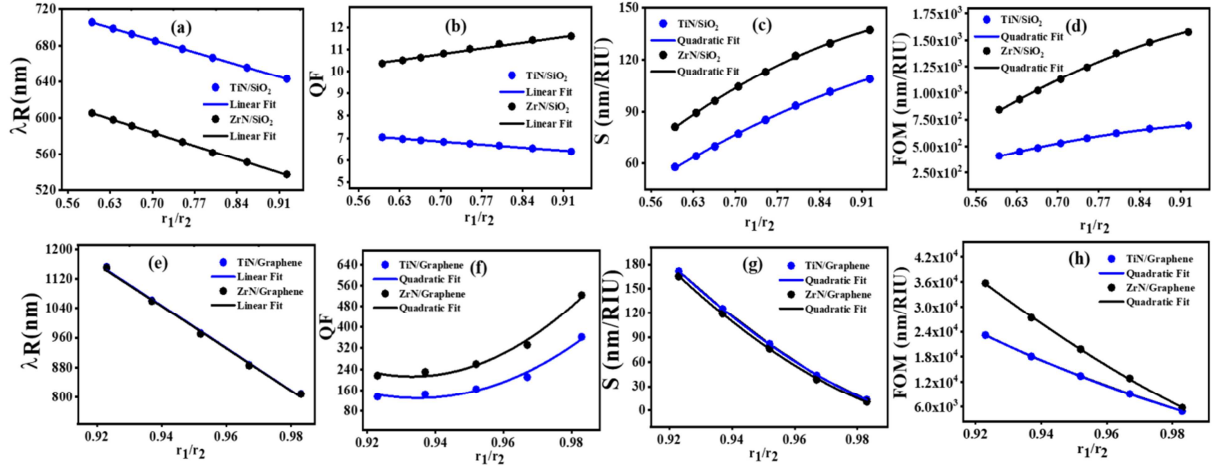


Fig. 9: Calculated (solid line) variation of λ_R , QF, S and FOM for (a-d). TiN/SiO₂, and ZrN/SiO₂ CSNP as a function of aspect ratio (r_1/r_2). Also shown is the polynomial fitting (circles), (e-h). TiN/Graphene and ZrN/Graphene CSNP as a function of aspect ratio (r_1/r_2). Also shown is the polynomial fitting (circles). The refractive index of embedding medium is 1.339 and T=300 K.

Graphene vs. Silica Coated Refractory Nitrides based Core-Shell Nanoparticles for Nanoplasmonic Sensing

Alok Singh and Manmohan Singh Shishodia

HIGHLIGHTS

Highlights for the manuscript entitled, **“Graphene vs. Silica Coated Refractory Nitrides based Core-Shell Nanoparticles for Nanoplasmonic Sensing”** may be summarized as follows:

- [1]. In view of the remarkable plasmonic properties of refractory nitrides (*e.g.*, ZrN and TiN) like higher degree of spectral tuneability, growth compatibility, high melting point, inherent CMOS and biocompatibility etc., and reported high surface area, excellent bio-molecular compatibility, improvement in the speed, higher sensitivity in graphene, the manuscript assess the feasibility of graphene coated refractory nitrides based core-shell nanoparticle as an efficient plasmonic sensor.
- [2]. To the best knowledge of authors, the manuscript present the first time investigation of graphene assisted refractory nitrides (TiN and ZrN) based core-shell nanoparticles.
- [3]. The manuscript reports that, (I). the plasmonic resonance wavelength can be fine tuned by controlling aspect ratio of core-shell nanoparticle, (II). aspect ratio can be optimized to obtain best sensitivity and figure of merit, (III). graphene coated core-shell nanoparticle produces higher sensitivity and figure of merit compared to that of dielectric coated core-shell nanoparticle, (IV). ZrN exhibit sensing characteristics superior than that of TiN, (V). sensing characteristics are more sensitive to the graphene layer compared to the case of dielectric.
- [4]. The fitting expressions useful for designing graphene/silica assisted core-shell nanoparticles based plasmonic sensor are presented.
- [5]. Graphene assisted core-shell nanoparticle based sensor exhibit higher sensitivity and figure of merit compared to that of silica.
- [6]. It is reported that the sensitivity=171.68 (nm/RIU) and figure of merit= 3.57×10^4 (nm/RIU) can be attained without optical gain incorporation.
- [7]. Rigorous analysis based on Mie scattering theory has been done. The results have been validated using FEM based COMSOL software also.

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CONFLICT OF INTEREST

April 05, 2020

To,

The Editor

Physica-E

Low dimensional Systems and Nanostructures

Dear Editor,

This is to certify that for manuscript entitled, “Graphene vs. Silica Coated Refractory Nitrides based Core-Shell Nanoparticles for Nanoplasmonic Sensing”, by Alok Singh, and myself (corresponding author) for publication in Physica-E; Low dimensional Systems and Nanostructures, there is no CONFLICT OF INTEREST.

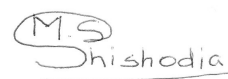
If any additional information is needed, please contact me by

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Thanking You.

Yours Sincerely



Dr. Manmohan Singh Shishodia
(Assistant Professor)