Modelling and simulation of surface plasmon resonance breathe acetone sensor based on doped polyaniline–graphene composite

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Abstract. Surface plasmon resonance (SPR) sensors are the best optical sensors. They are very sensitive to a slight change in refractive index/dielectric constant at the interface of metal/dielectric materials. Gold and silver are the commonly used plasmonic materials. However, the materials show reasonable losses at some spectral range of interest. This paper presents the modeling and simulation of an SPR breathe acetone sensor based on tunable doped polyaniline-doped graphene composite at mid infrared range. Graphene has shown the capability of shrinking 3000nm wavelength of light to 54.7 nm with very negligible imaginary dielectric constant (0.43). The high negative effective dielectric constant of the polyaniline/graphene composite (-33.5) is very promising for developing SPR based sensing devices. The composite based SPR curve shows a promising SPR shift (almost 10 º) due absorption of acetone vapour/exhale breathe acetone. It also shows better SPR curve features mid infrared spectral range compared to that of the gold and silver at visible range (Their optimum range). Therefore, this SPR sensor can realize the non-invasive, sensitive and selective detection of exhale breathe acetone for screening for diabetes at mid infrared range.

1. Introduction
Diabetes is a chronic disease that occurs when human body can no longer appropriately regulate blood sugar. It can lead to many complications in the human body. Unfortunately, the number of diabetics is rapidly increasing even beyond statistical predictions globally. This has been attributed to the population growth, aging, urbanization, increasing occurrence of obesity, lack of awareness, unavailability of simple monitoring devices and physical inactivity [1]. Simple, reliable and proper means of diagnosis can help in mitigating the rapid increase. Currently diabetes is diagnosed through blood glucose test. Unfortunately, the method requires trained personnel, consumes time, laboratory restricted usage and invasive procedures [2]. Exhale breathe acetone has been identified as a good biomarker that can provide a non-invasive detection of diabetes [3]. Acetone concentration in the human exhale breathe is generally very low (0.1 ppm - 0.8 ppm), and it might be high in the case of metabolism disorders, including diabetes mellitus (DM) (1.8 ppm – 5.0 ppm)[4].
Since the recognition of exhale breath acetone as the diabetes biomarker, a lot of researches have been conducted on its detection [5, 6]. The conventional means of acetone detection includes gas chromatography – mass spectrometry (GC-MS), selected ion flow tube mass spectrometry (SIFT-MS), proton transfer reaction mass (PTR-MS), high performance liquid chromatography (HPLC), ion mobility spectrometry (IMS), plus laser techniques like tunable diode laser absorption spectroscopy (TDLAS) and cavity ring down spectroscopy (CRDS). These instruments are capable of detecting trace levels of acetone vapour with better sensitivity and selectivity, relatively. However, they rely on sophisticated instrumentation, complicated sample collection methods, and can only be afforded by advanced medical institutions [7].

Fortunately, the detection of exhale breathe acetone via biosensors possess better promising features. Easy and real time non-invasive detection is possible with biosensors. A biosensor is an analytical device that can detect a biological analyte and convert its response into an electrical signal [8]. Most of the exhale breathe acetone biosensors use metal oxide semiconductors as the sensing layer (mostly based on chemiresistive transduction method) [9-11]. But, metal oxide chemiresistive biosensors suffer high operational temperature [11]. Contact resistance influence also results in unreliable selectivity [12]. Furthermore, the humidity influence is another issue of concern [9, 13]. In addition, most of the fabrication processes for these sensors are complicated; incorporating non-easy to find materials, difficult to process and synthesis materials and features poor biocompatibility.

Optical based biosensors are the best alternatives because of their promising greater sensitivity, electrical passiveness, freedom from electromagnetic interference, wide dynamic range, nonrequirement of reference electrode, potential for higher-information content and multiplexing capabilities [13]. Surface Plasmon Resonance (SPR) based sensors has been identified among the best optical biosensors [14]. It measures analyte concentration by exploiting the change in the refractive index at the interface of metal/heavily doped semiconductor-dielectric interface. When a light source is incident on a metal/heavily doped semiconductor-dielectric interface, after total internal reflection, a drop is observed in the intensity of the reflected light at a particular angle called SPR angle. Presence of a biomolecule (analyte) or any other material at the vicinity of the dielectric medium shifts the SPR angle which is called dip.

It is quite advantageous and interesting that many biomolecules including acetone have characteristic absorption wavelength which mostly occurs at mid infrared range [15]. This can provide a highly selective and sensitive detection. Unfortunately, the conventional plasmonic materials (e.g. Au, Ag, Cu, Al, etc.) are good only at visible and near infrared range [15]. They possess reasonable loss at other spectral range of interest and, in addition, cannot be tuned. Doped polyanile and doped graphene are very promising plasmonic materials with unique and interesting features at mid infrared range [16]. In this paper, an SPR breath acetone sensor for diabetes screening and monitoring, based on the composite of doped Polyaniline (PANI)/graphene as the mid infrared plasmonic material, is modelled and simulated. The performance of this novel composite material is assessed by comparing it with that of the most commonly used conventional plasmonic materials based on Au and Ag.

2. Mathematical Modelling And Simulation

The modeling of surface plasmon resonance sensors requires the identification of some basic parameters. One important parameter is the dielectric constant of the materials used in SPR bio-sensor proposed in this research which are listed in Table 1. The mid infrared dielectric constant of doped polyaniline is extracted from the work of [17]. It shows true metallic state that can that can be analyzed using the Drude model. This was a result of heavy doping with Carphor sulfonic acid. For graphene, its dielectric constant is hard to be expressed directly. The common method is to deal with the conductivity from the Kubo formula [18], which in the case of this study (doped graphene and low energy consideration), only intra-band contribution is being considered using equation 1. The dielectric constant of the doped graphene can then be calculated using equation 2. Substituting equation 1 in equation 2 give rise to the overall dielectric constant equation (equation 3). For the
composite, the effective dielectric constant was calculated using Maxwell-Gannett equation (equation 4). The remaining important parameters in Table 1 were obtained from [19, 20].

\[
\alpha_{\text{intra}} = \frac{e^2 \mu}{\pi h^2} \left( \frac{i}{\omega + \tau} \right)^{-1}
\]

(1)

\[
\varepsilon_{\text{gr}} = 1 + \frac{i}{\varepsilon_0 \omega t_g} \alpha_{\text{intra}}
\]

(2)

\[
\varepsilon_{\text{gr}} = \varepsilon_r - \left( \frac{\mu e^2 \omega}{\pi h^2 \left( \omega^2 + \tau^2 \right)^2} \right) \frac{1}{\omega \varepsilon_0 t_g} + i \left( \frac{\mu e^2}{\pi h^2 \left( \omega^2 + \tau^2 \right) \tau} \right) \frac{1}{\omega \varepsilon_0 t_g}
\]

(3)

\[
\varepsilon_{\text{eff}} = \frac{1 + 2 f_{\text{gr}} \left( \frac{\varepsilon_{\text{gr}} - \varepsilon_{\text{PANI}}}{\varepsilon_{\text{gr}} + 2 \varepsilon_{\text{PANI}}} \right)}{1 - f_{\text{gr}} \left( \frac{\varepsilon_{\text{gr}} - \varepsilon_{\text{PANI}}}{\varepsilon_{\text{gr}} + 2 \varepsilon_{\text{PANI}}} \right)}
\]

(4)

Where, \( \alpha_{\text{intra}} \) is the intraband conductivity, \( e \) is the elementary charge, \( \mu \) is the chemical potential, \( h \) is the reduced Planck's constant, \( \omega \) is the frequency, \( \tau \) is the scattering lifetimes, \( t_g \) is the thickness of the graphene, \( \varepsilon_{\text{gr}} \) is the dielectric constant of graphene, \( \varepsilon_{\text{eff}} \) is the effective dielectric constant of the doped PANI/graphene composite, \( \varepsilon'_{\text{PANI}} \) is the real part dielectric constant of doped PANI, \( \varepsilon_0 \) is the free space permittivity and \( f_{\text{gr}} \) is the fractional volume of the graphene. In order to achieve high doping, 0.8 eV and 0.2 ps has been selected as the values for \( \mu \) and \( \tau \) respectively.

**Table 1.** Dielectric constant of the materials of the SPR based breathe acetone biosensor.

| Material                        | Real dielectric constant | Imaginary dielectric constant | Refractive index |
|--------------------------------|--------------------------|-------------------------------|------------------|
| Doped PANI                     | -30.62                   | 2                             | -5.5             |
| Doped graphene                 | -51.86                   | 0.43                          | 1.5              |
| Acetone                        | 1.25                     | 0                             | 1.12             |
| Air                            | 1.00                     | 0                             | 1.00             |
| Calcium fluoride prism (CaF₂)  | 2.1                      | 0                             | 1.45             |
| Effective dielectric constant of composite | -33.5                   | 1.95                          | -                |

The SPR modelling considers three most important SPR parameters. These are the SPR wavelength (\( \lambda_{\text{SPR}} \)), propagation length (\( \delta_{\text{SPR}} \)) and penetration depth (\( \delta \)) as shown in equations 5, 6 and 7, respectively. The subscript a-c in the equations represents doped PANI, doped graphene and dielectric medium respectively. Every good SPR biosensor is expected to possess long propagation length and short penetration depth through the dielectric. The former indicates how low loss is the plasmonic material while the later indicates the confinement ability. The SPR modelling equations were treated individually for both the doped polyaniline (PANI) and the doped graphene. The SPR based breathe acetone biosensor based on the modelled materials was later simulated.
The simulation was conducted using Fresnel equations based WinSpall SPR simulation software. Because of the characteristic absorption of some biomolecules (breathe acetone inclusive) at mid infrared frequencies, mid infrared wavelength (3000nm) and triangular prism options have been selected for the simulation in the case of the doped PANI/graphene composite. The result of an SPR sensor based on most used plasmonic materials (gold and silver) has been compared with that of the composite.

\[
\lambda_{SPR} = \lambda_0 \left[ \frac{\varepsilon_d + \varepsilon_{PANI}}{\varepsilon_d \varepsilon_{PANI}} \right]^{1/2} 
\]

(5a)

\[
\lambda_{SPR} = \frac{\lambda_0 \left( 4\alpha E_F \right)}{\hbar \omega (\varepsilon_r + 1)} 
\]

(5b)

\[
\lambda_0 \left( \varepsilon_{PANI} \right)^{2} \left[ \frac{\varepsilon_d + \varepsilon_{PANI}}{\varepsilon_d \varepsilon_{PANI}} \right]^{3/2} 
\]

(5c)

\[

\left( \delta_{SPR} \right) = \frac{2\pi \varepsilon_{PANI}}{\lambda_0 \left( \varepsilon_{PANI} \right)^{2}} 
\]

(6a)

\[

\left( \delta_{SPR} \right) = \frac{\lambda_0 \left( \tau \alpha E_F \right)}{\pi \hbar (\varepsilon_r + 1)} 
\]

(6b)

\[

\delta_a = \frac{\lambda_0 \left[ \varepsilon_d + \varepsilon_{PANI} \left( \varepsilon_{PANI} \right)^2 \right]}{2\pi} 
\]

(7a)

\[

\delta_b = \frac{\lambda_{SPR}}{2\pi} 
\]

(7b)

\[

\delta_c = \frac{\lambda_0 \left[ \varepsilon_d + \varepsilon_{PANI} \left( \varepsilon_{PANI} \right)^2 \right]}{2\pi} 
\]

(7c)

Where, \( \lambda_0 \) is the free space wavelength, \( \varepsilon_d \) dielectric constant of the dielectric medium, \( \alpha \) is the fine structure constant (\( \approx 1/137 \)), \( E_F \) is the Fermi energy level (\( E_F \approx \mu \)) and \( \varepsilon_r \) is the dielectric constant of the substrate.

3. Result and Discussion
The result for the modeling and the simulation of an SPR based biosensor for monitoring and screening of diabetes has been explored in an organized way. SPR features have been investigated in doped PANI and doped graphene separately at mid infrared spectral range. The effective dielectric constant of the composite was later employed in the simulation of the SPR based device. As stated, an ideal SPR based biosensor requires a plasmonic material with no or very less loss and light confinement capability at frequency of interest. These necessitate the requirement of large negative real dielectric constant and zero or very low imaginary dielectric constant respectively. From Table 1 and 2, both the doped PANI and Doped graphene proved to be promising mid infrared plasmonic materials for biosensing application. Both possess large negative real and small imaginary dielectric
constants. The light confinement capability is well explained by the values of SPR wavelength, penetration depth and dielectric constants in Table 2. The 3000nm free space wavelength has been confined to 2.95 µm and 54.7 nm for the doped PANI and doped graphene respectively. This shows that even if the confinement light in doped PANI is not that good, the confinement from its graphene (which shrink 3000 nm wavelength of light to 54.7 nm) based composite can be very promising. Critical look at the values of penetration depths, propagation length and imaginary dielectric constants; show how the loss can be mitigated from the individual contribution of materials of the composite. Further understanding and the confirmation for the realisation of this promising SPR based is shown in the simulation result. The simulation based on Fresnel equation has been conducted using WinSpall software. A huge shift in SPR angle (from about 45° to around 50°) has been observed due to absorption of very negligible amount of acetone vapour (simulating exhale breathe acetone) on the surface of the sensing layer (Figure 1). The shift was simulated by assuming the alteration to dielectric constant in the dielectric medium to be only 0.25. The curves also feature sharp curves that can allow accurate determination of even a minute shift.

### Table 2. SPR modelling result.

| Parameter                                             | Result   |
|-------------------------------------------------------|----------|
| SPR wavelength (\(\lambda_{SPR}\)) - Doped PANI      | 2.95 µm  |
| SPR wavelength (\(\lambda_{SPR}\)) - Doped graphene   | 54.7 nm  |
| Propagation length (\(\delta_{SPR}\)) - Doped PANI    | 214.85 µm|
| Propagation length (\(\delta_{SPR}\)) - Doped graphene| 546 nm   |
| Penetration depth through Doped PANI (\(\delta_{PANI}\)) | 88 nm    |
| Penetration depth through dielectric (\(\delta_{d}\)) | 2.68µm   |
| Penetration depth through doped graphene (\(\delta_{gr}\)) | 8.71 nm  |
| Intraband conductivity of doped graphene (\(\sigma_{int\sigma}\)) | 7.4 x 10^13 S/m |
| Real part dielectric constant of doped graphene       | -51.86   |
| Imaginary part dielectric constant of doped graphene  | 0.43     |

In order to show the betterment of this proposed biosensor, figure 2 has illustrated the comparison between the composite based SPR curves and that of the most common conventional SPR materials (gold and silver). The composite based SPR shows sharper curve. This provides the evidence that this composite can be better than both gold and silver SPR based biosensor. The sharpness of curves indicates greatness in terms of sensitivity and accuracy.

\[
\text{Sensitivity} = \frac{\text{shift}}{\Delta R.I} \quad \text{(8)}
\]

\[
\text{Accuracy} = \frac{\text{shift}}{\text{FWHM}} \quad \text{(9)}
\]

Where the shift means the shift in SPR curve, \(\Delta R.I\) is the refractive index change and FWHM is full width at half maximum.

From sensitivity point of view (equation 8), it can be understood that the sensitivity is better with the sharp curves (composite based SPR curve) as oppose to less sharp once. Also, the FWHM tends to be smaller with sharp curves. This implies greatness in terms of accuracy.
Therefore, using this composite as alternative plasmonic material in SPR based sensors is important in number of ways. Its tunability would allow the shifting of its plasma frequency to mid infrared spectral range. More importantly, mid infrared operation improves selectiviy in the detection of breathe acetone due to its characteristic absorption frequency.

4. Conclusion
This paper present the modelling and simulation of an SPR based breathe acetone biosensor for monitoring and screening of diabetes. Novel plasmonic materials have been proposed. The possession of low dielectric loss by materials, 2 and 0.43 for the doped PANI and the doped graphene shows how promising is the biosensor. The effective real part and imaginary part passes the SPR criterion, possession of -33.5 and 2 (large negative real part and small imaginary part) respectively. Simulation has indicated a huge shift due to absorption of small amount of acetone vapour (45° to around 50°) (Figure 1). The better SPR curve of the composite proves the advantages of this biosensor over gold and silver based (Figure 2). This would no doubt help in the proper and reliable monitoring and screening of diabetes with better sensitivity and accuracy.

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