Selecting silver nanoshells for colorimetric sensors

Raphael M. S. M. Baltar
Federal Institute of Education, Science and Technology of Maranhão
PPGEE, Federal University of Pernambuco
Recife, Brazil
raphael.baltar@ifma.edu.br

Renato E. de Araujo
Laboratory of Biomedical Optics and Imaging
Federal University of Pernambuco
Recife, Brazil
renato.earaujo@ufpe.br

Sajid Farooq
Center for Lasers and Applications
Instituto de Pesquisas Energeticas e Nucleares, IPEN — CNEN
Sao Paulo, Brazil
sajiddahar@gmail.com

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***Abstract*—In this work the use of silver nanoshell as a starting point for the establishment of colorimetric sensor platforms, under solar illumination, was evaluated. Mie theory was explored on the analysis of the nanosensor linearity and sensitivity, considering 4 different color spaces and the influence of the nanoshell geometry. A high performance plasmonic nanoplatform was identified. The nanosensor platform based on nanoshells, with 35 nm SiO_2 core radius and 25 nm Ag shell thickness, showed sensitivity values up to 2.78 RIU^{-1} and linearity higher than 0.96, considering the Hue parameter of the HSV color space. The identification of optimized plasmonic nanoplatforms may extend the use naked-eye colorimetric applications in low-resource environments.**

***Index Terms*—Optical sensors; Nanotechnology; Plasmonics**

I. Introduction

Metallic nanostructures are important starting points for the development of optical sensor platforms. The interaction of light with metallic nanostrucutres may lead to a phenomenon known as Localized Surface Plasmon Resonance (LSPR), governed by the collective coherent oscillations of free electrons. The LSPR spectrum is reliant on shape, size, material of the nanoparticle (NP) and, as well, on the surrounding dielectric medium refractive index [1]. In principal, LSPR can be achieved in any metal by fulfilling the Frohlich condition: $\epsilon_r = -2\epsilon_m$ [2], where ϵ_r is the real part of the nanoparticle complex dielectric function and ϵ_m is permittivity of the NP surrounding non-absorbing medium. Gold and silver are the mostly used metals, with negative real dielectric values, on LSPR applications [3].

LSPR sensors are explored in wide variety applications, as in medical diagnosis and chemical identification. In general, LSPR sensors are based on the identification of the LSPR spectrum shift, induced by the modification of the environment refractive index (RI).

Several examples of plasmonic sensor and biosensors were described in the literature, revealing that the spherical NPs-base platforms show high bulk sensitivity [5]. By exploring silver nanospheres adhered on a glass slide and functionalized with monoclonal anti-Candida antibodies, Farooq et al. demonstrated by the identification of Candida albicans antigen [6]. LSPR molecular sensing, based on gold nanospheres was also for the dengue diagnosis in the acute phase of the infection [7], [8]. Furthermore, based on optimization analysis of 40 nm SiO_2/ 5nm Au core-shell particles, Farooq et al. showed that high sensitivity values could be reached with spherical nanoparticles [3]. In particular, SiO_2/Au core-shell nanoplatforms can reach sensitivity values about 4x higher than massive Au nanospheres, indicating that nanoshells (NS) are suitable as starting-point for the development of high performance nanostructured sensors. LSPR peak of gold nanoshells can tuneble from red to infrared by changing shell thickness or radius. Moreover, silver nanoshell allows the establishment of plasmonic peak at the visible spectrum.

The spectral analysis of LSPR nanoplatforms requires the use of instrumentation resources, as spectrometers, which my limit the use of plasmonic sensors in low resource environments. However, plasmonic sensing platforms can also be developed to be explored with a naked-eye approach, in which LSPR peak variation allows visual identification of refractive index changes or molecular binding events.

LSPR colorimetric sensors may exploit ‘aggregation’ or ‘non-aggregation’ detection strategies [12]. In general, solution-based platforms that use NP aggregation approach show high sensitivity for chemical or molecular identification. The NP aggregation induces significant shifts on the LSPR peak of the colloidal platform, which can be identify by naked-eye. However, colloidal nanoparticle stability may restricts the use of the solution-based platforms. Alternatively, the use of surface-base platforms, exploring a ‘non-aggregation’ strategy, is considered as a robust approach for the development of LSPR sensor.

Recently, Reinhard et al. described a methodology for optimizing nanospheres design for colorimetric sensors [13]. For that, colorimetric sensitivity, η_c, is defined as the ratio of the color space coordinate changes as a function of the variation of the medium refractive index. Therefore, η_c is given

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by:

$$\eta_c = \frac{\Delta y}{\Delta n_m}, \tag{1}$$

where Δy is the intensity variation of a given color component y induced by a medium refractive index change, Δn_m. In addition, in reference [13], a detailed comparative analysis of the designed nanoplatform colorimetric sensitivity in five different color spaces were performed. There was found that gold nanospheres could lead to η_c values up to 1.4 RIU^{-1}, based on the variation of the hue angle values at HSV color space caused by the medium RI change. However, some fundamental aspects of plasmonic colorimetry were not fully explored in [13], such as the influence of the light source and shape of the nanostructure.

In this work we evaluate the use of SiO_2 core/silver shell nanoparticles as a starting point for the establishment of a colorimetric sensor platform, under solar illumination. In addition, a theoretical approach is explored on the analysis of the nanosensor linearity and sensitivity, considering 4 different color spaces and the influence of the NS geometry.

II. Methodology

In this work, the absorption, scattering and extinction cross sections (θ_{abs}, θ_{sca} and θ_{ext}, respectively) of the nanoshells were obtained using the computational package PyMieScatt [14]. For the spectroscopic analysis, the NS core radius varied from 10 to 50 nm and the shell thickness from 5 to 35 nm. The permissiveness values of Ag were obtained from Johnson & Christy [15]. Considering a CIE D65 illuminant (average daylight in the northern hemisphere with a color temperature of 6500K), the scattered and absorbed light spectrum from the Ag NS were calculated. From the extinction spectra of the metallic nanoshell, the tristimulus values (X, Y, and Z) of the CIE XYZ color space were obtained, according to [13]:

$$\begin{aligned} X &= \frac{\int_{360}^{830} CIE\bar{x}(\lambda) \times D65(\lambda) \times 10^{-A(\lambda)} d\lambda}{\int_{360}^{830} CIE\bar{y}(\lambda) \times D65(\lambda)} \\ Y &= \frac{\int_{360}^{830} CIE\bar{y}(\lambda) \times D65(\lambda) \times 10^{-A(\lambda)} d\lambda}{\int_{360}^{830} CIE\bar{y}(\lambda) \times D65(\lambda)} \\ Z &= \frac{\int_{360}^{830} CIE\bar{z}(\lambda) \times D65(\lambda) \times 10^{-A(\lambda)} d\lambda}{\int_{360}^{830} CIE\bar{y}(\lambda) \times D65(\lambda)} \end{aligned} \tag{2}$$

where $CIE\bar{x}$, $CIE\bar{y}$ and $CIE\bar{z}$ are the 2-degree standard observer color matching functions for XYZ (based on experimental data collected by Wright and Guild [16]), D65(λ) is the illuminant spectrum and A is the sensor platform absorbance, which is proportional to σ_{ext}. The platform absorbance was set to 0.1 for all NS configuration. By knowing the tristimulus, the 12 color parameters (R, G and B; r, g and b; S, H and V; L, A and B) from the sRGB, rgb, HSV and CIE LAB were obtained [13], i.e., three color components (y) were evaluated for each color space used.

Considering the medium refractive index changing from 1.33 to 1.43 RIU, the nanoplataform colorimetric sensitivity were analysed for each color component, according to equation 1. The linearity of the colorimetric sensitivity was also apprised, by weighting the R-squared (R^2) of each color space component variation. Here, only nanoplatforms with $R^2 \geq 0.96$ were considered suitable for sensing purpose.

III. Results and Discussion

The LSPR spectrum of NS is reliant to is geometry (core diameter and shell thinness). Figures 1 depicts the extinction, absorption and scattering cross-sections of the NS with a 35 nm SiO_2 radius and Ag shell thickness of 20 nm, in water (RI = 1.33). The Ag nanostructure presents LSPR peak at approximately 520 nm and a broad extinction spectrum, which is mainly governed by scattering. Increasing the NS core radius, the LSPR peak red-shifts. On the other hand, increasing the NS Ag layer thickness the LSPR peak shifts towards lower wavelengths.

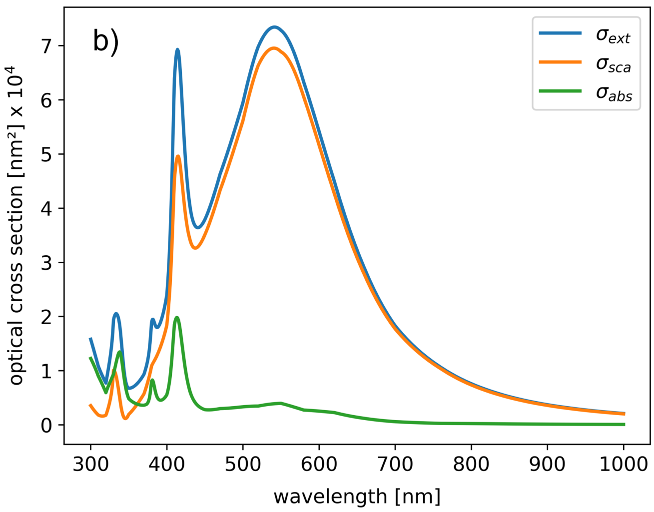

Fig. 1. Extinction, absorption and scattering cross sections for silver NS in water

The colorimetric sensitivity analysis of silver NS platform subjected to the D65 illuminant is shown in Figure 2, in which several NS configurations were evaluated. The highest colorimetric sensitivity values were achieved by the Hue color parameter of HSV color space. The highest colorimetric sensitivity (η_c = 6.29 RIU^{-1}) were obtained for NS with 30nm of radius and 35nm of shell thickness. Nevertheless, this high colorimetric sensitivity NS configuration do not meet the defined linearity criterion ($R^2 > 0.96$).

The linearity of the colorimetric sensor is analysed by evaluating the behavior of the color component as function of refractive index changes (as shown in Figure 3) and quantified by the R^2 parameter. Considering the linearity criterion

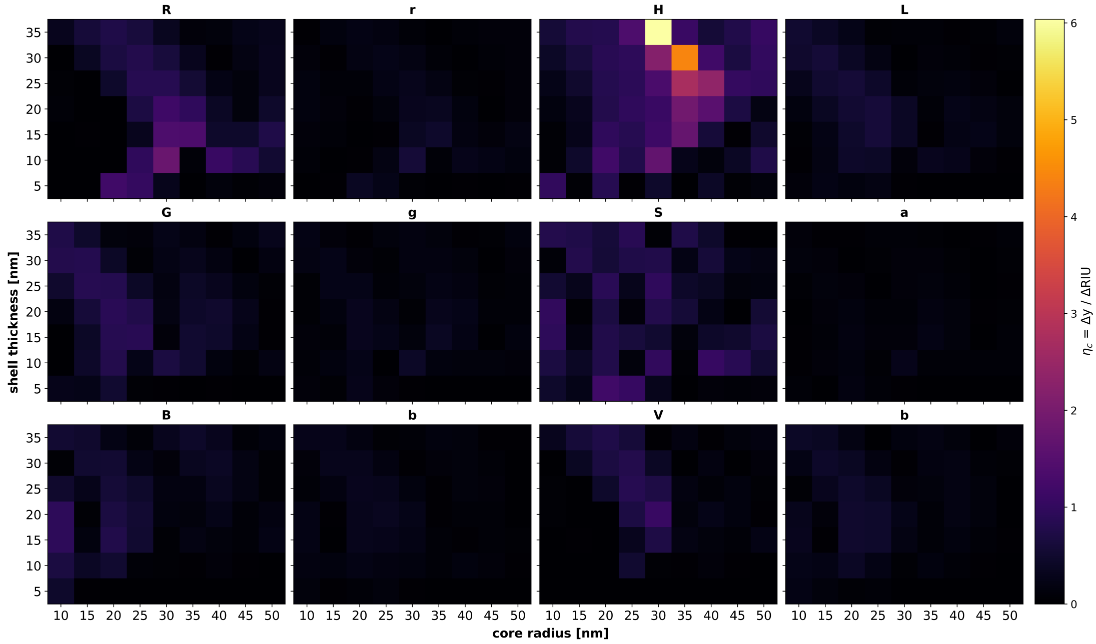

Fig. 2. Colorimetric sensitivity values of the plasmonic sensor platform, for the D65 illuminant and RI range of 1.33 a 1.43, as function of the NS radius and thickness.

($R^2 > 0.96$), the highest colorimetric sensitivity value were found for a 35 nm core radius/25nm Ag shell thickness NS under D65 illuminant, exploring the Hue color component of HSV color space. Figure 3 indicates $R^2 = 0.98$ and a high colorimetric sensitivity value, $\eta_c = 2.78$ RIU^{-1}, which is 198% higher than the reported by Reinhard et al. ($\eta_c = 1.4$ RIU^{-1}) from bare nanospheres with radius of approximately 91 nm, D65 illuminant and color component Hue) [13].

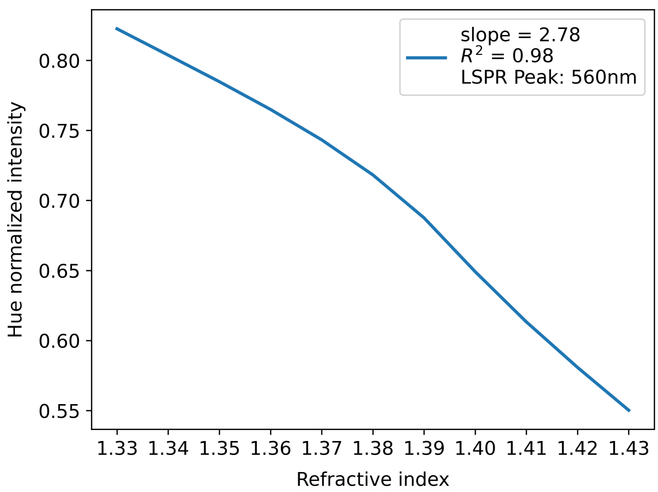

Fig. 3. Normalized Hue color component values for a 35 nm core radius/25nm Ag shell thickness NS under D65 illuminant.

IV. Conclusion

The naked-eye high performance colorimetric sensors find applications in different fields. Here Mie theory was explore to identify the optimized nanoshell configuration for plasmonic colorimetric sensor platform. For a D65 illuminant, a nanosensor based on a NS with 35 nm SiO_2 core radius and 25 nm Ag shell thickness showed $\eta_c = 2.78$ RIU^{-1} and $R^2 = 0.98$, considering the H parameter of the HSV color space. The colorimetric platform exploring optimized Ag NS reached sensitivity values 198% higher than the nanoplatform based on gold nanospheres presented in [13]. The colorimetric sensor performance is greatly influenced by the illuminant, which may limits the use of the nanoshell platform. Moreover, the identification of optimized sensing nanoplatforms may extend the use naked-eye colorimetric applications in low-resource environments.

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