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Characterization of AuNPs+rGO as a functionalized layer for LSPR sensors

Alessandro Fantoni [a,b,*], Vladan Stojkovic [a], Ana Carvalho [d], Ana P.C. Ribeiro [c], Elisabete C.B.A. Alegria [c,d]

[a] ADEETC-ISEL-Instituto Politécnico de Lisboa, 1949-014 Lisbon, Portugal
[b] CTS-UNINOVA, Caparica, Portugal
[c] CQE-Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisbon, Portugal
[d] ADEQ-ISEL-Instituto Politécnico de Lisboa, 1949-014 Lisbon, Portugal

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ABSTRACT

Graphene-based materials have been extensively explored in recent years as valuable candidates as the key material for novel structures in the field, among many other applications, of sensing devices. This work reports a study about the applicability of rGO as a support for gold nanoparticles (AuNPs) prepared with an economic and eco-friendly method using phytochemicals present in tea extract at room temperature. The overall analysis is supported by simulation results about the LSPR effect in AuNPs-rGO, obtained by Mie theory and FDTD method. The residual phytochemicals are analysed as capping agent of the nanoparticles and their influence on the LSPR properties of the nanoparticles is outlined. The resulting composite is suitable for application as a low-cost sensing layer in biomedical LSPR sensor devices.

1. Introduction

There is a growing interest in modern health challenges for accurate diagnostic laboratory tests in situations where access to analytic laboratory facilities are not available. Moreover, in developed countries, specific analysis has a price unacceptably high for the public health system to support systematic screening of the risk population impacting on disease prevention. It is therefore advisable the development of a portable and low-cost system allowing point-of-care diagnostic. There is a growing expectation from the medical community in this area [1], and the requirements for these lab-on-chip systems are to be inexpensive, rugged, accurate and reliable [2,3]. Great progress in label free biosensors based on Local Surface Plasmon Resonance (LSPR) have been reported [4,5]. The advantage of this class of sensor devices is the reduced dimension, possible integration with standard electronic systems and opportunity of producing proteomic multiplexed output [6]. While it is possible to obtain great accuracy in the results produced by nanoplasmonic biosensors [7], the production costs remain still high, mainly for requiring nonstandard production techniques. This work presents an approach to a low-cost sensor device based on the LSPR effect. The active sensing layer is a composite of gold nanoparticles, embedded in a matrix of reduced graphene oxide (AnNPS+rGO). Light transmitted across this layer is governed by the LSPR interaction of Au nanoparticles, whose useful wavelength spectrum is located at 500–700 nm range, which is the part of the spectrum where spectral responsivity of Pressure Enhanced Chemical Vapour Deposition (PECVD) thin film photodiodes [8], is optimal. This condition allows an integrated device whose optoelectronic readout is performed by an amorphous silicon photodiode that by measuring the spectral photocurrent can monitor light transmission properties of the AuNPs+rGO layer and intensity of the LSPR effect following a wavelength interrogation scheme. The structure of the proposed device is reported in Fig. 1. The present work deals with simulation results, about the plasmonic properties of the AuNPs+rGO layer, including the effect of including residuals of the reduction component used in the preparation of the Au nanoparticles.

2. The AuNPs+rGO layer

The AuNPs+rGO layer has been prepared using an economic alternative and eco-friendly synthetic method, at room temperature. While green synthesis method for metal nanocomposites has been also recently successfully used for production of various

* Corresponding author at: ADEETC-ISEL-Instituto Politécnico de Lisboa, R. Conselheiro Emídio Navarro 1, 1959-007 Lisbon, Portugal.
E-mail address: afantoni@deetc.isel.ipl.pt (A. Fantoni).

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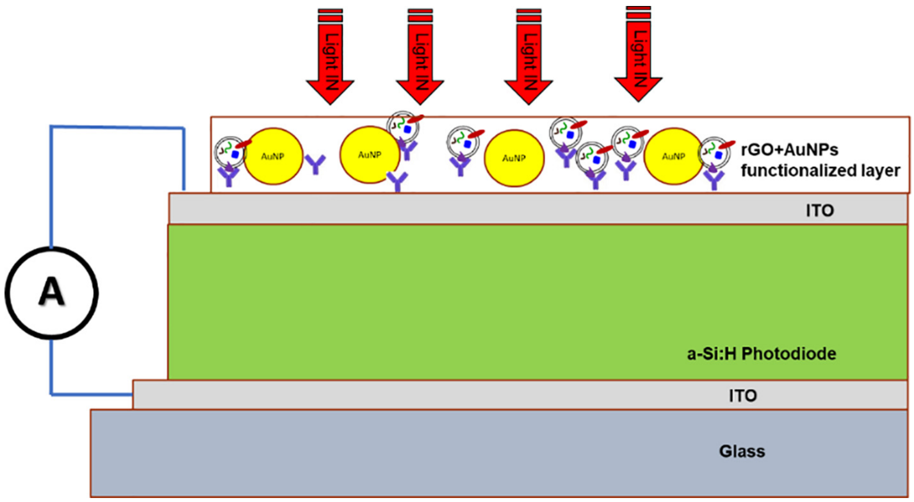

Fig. 1. Schematics of the LSPR sensor based on rGO+AuNPs. Yellow circles: AuNPs, Y shapes: antibodies. Small white circles: biomarkers trapped by the antibodies. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

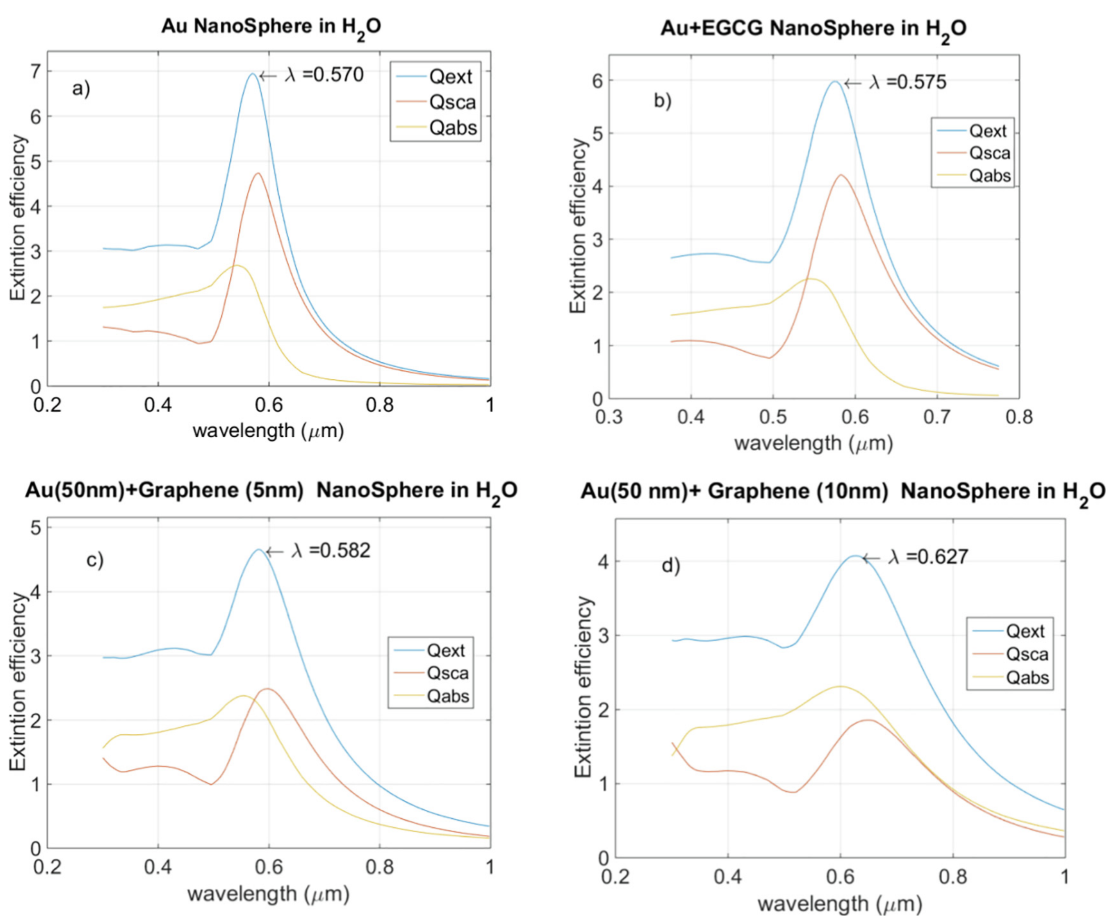

Fig. 2. Light extinction and LSPR effect produced by an AuNP with 50 nm radius diluted in water (a), capped with a 5 nm layer of EGCG (b), covered by a thin layer of rGO (c), capped with a 5 nm layer of EGCG and covered by rGO (d).

metal oxides nanoparticles [9], the green method used in this work for AuNPs synthesis targets the production of a low cost and disposable sensor device, using a metal salt ($HAuCl_4$) and phytochemicals present in tea extract as both the reducing and capping agent [10]. The LSPR effect is visible and the central wavelength for the LSPR depends on the rGO concentration [11]. The presence of rGO results in a general reduction of light transmission over the entire spectrum, in comparison to the solutions containing exclusively AuNPs. Like for other carbon-based materials [12]. The effect of rGO is to support the AuNPs anchoring,

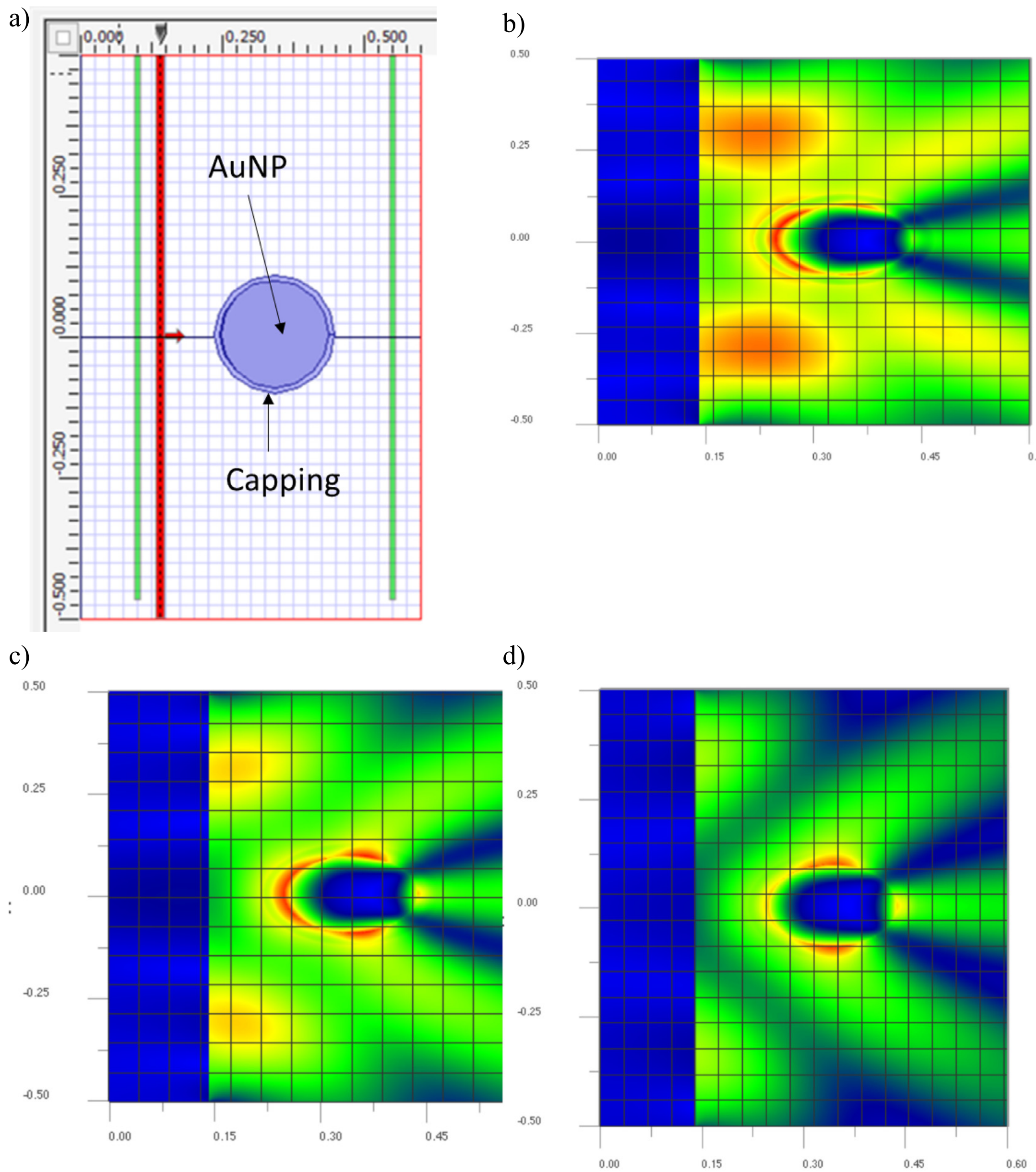

Fig. 3. Layout of the FDTD simulation domain (a) and electric field simulation around a AuNP with a 45 nm radius, covered by a thin layer (5 nm) of EGCG and an external recovering of rGO (10 nm). Light wavelength is 570 nm (b), 627 nm (c) and 700 nm (d). All dimensions in μm.

The central wavelength for LSPR is redshifted by the AuNPs-rGO coupling. The eco-friendly synthetic method leaves the resulting nanoparticles capped by a covering of residuals from tea polyphenols used as a reductive agent. The most abundant polyphenols encountered in tea is the Epigallocatechin gallate (EGCG) [13], whose reported refractive index is 1.857 [14]. The presence of this additional capping agent, in conjunction with the rGO matrix, affects the plasmonic properties of the nanoparticles. These effects are studied by a numerical simulation approach.

3. Simulation results

The LSPR has been simulated using a direct computation of the light extinction, based on the Mie Theory [15]. A Finite Differences Time Domain (FDTD) simulation has been used to analyse the scattered field in the space region surrounding the gold nanoparticle. We simulated the AuNPs in water, embedded in rGO and capped with a thin layer of EGCG. The light extinction profile and the LSPR effect produced by AuNPs with 50 nm radius diluted in water and capped with a 5 nm layer of EGCG is reported in Fig. 2.

The polyphenol effect is a reduced red shifting of the LSPR peak and a lowering of the light extinction maximum at the wavelength where the LSPR condition is verified. A similar effect was observed considering a capping of rGO around the nanoparticle. Increasing the rGO capping thickness, the LSPR peak becomes more broadened. The central wavelength for the LSPR remains in the visible range, as required by the spectral sensitivity of the amorphous silicon photodetectors. The FDTD analysis focuses the scattering behaviour, around the nanoparticle, of incident light with wavelength between 570 nm and 580 nm.

In Fig. 3 is depicted the simulated structure and the electric field value, obtained by FDTD simulation under different light wavelengths, of a gold nanoparticle with a radius of 45 nm, covered by a thin layer (5 nm) of EGCG and an external recovering

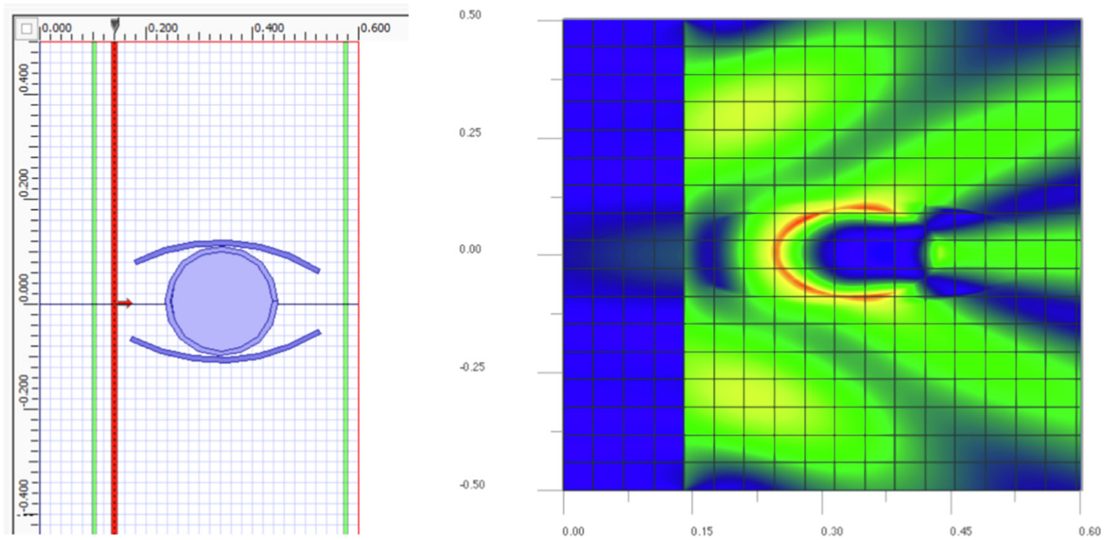

Fig. 4. FDTD simulation domain (a) and electric field simulation (b) of an AuNP capped by ECGC, posed on the wall of two rGO flakes. Light wavelength is 627 nm.

of rGO (10 nm). Light scattering produced under LSPR condition, at a wavelength of 627 nm, is much higher than in the other cases. The combination of the double layer capping appears to enhance the plasmonic effects of the AuNPs at the central wavelength.

The last simulation is based on the realistic assumption that in experimental samples, the AuNPs will be capped by polyphenols but even if their contact with the rGO flakes is not complete, it can be represented by some regions of localized contact as reported in Fig. 4. The simulation results show that even in this configuration, LSPR characteristics of AuNPs are maintained. These results point out that AuNPs, synthetized with tea polyphenols as reduction agent and embedded in a matrix or rGO, exhibit strong wavelength selective properties at the resonant LSPR condition in the red region of the spectrum, approximately at 627 nm. The results herby presented consider the LSPR produced by one nanoparticle, neglecting interferences with other neighbour particles. In real cases, one may expect AuNPs groups with different size to produce variable dimension aggregates. Anyway, the AuNPs production green method has been proved to produce nanoparticles uniform in size and shape [9]. Also, we expect the polyphenols layer to support the spacing between AuNPs, preventing mutual interference and multipolar behaviour.

4. Conclusion

Following the path toward the realization of for LSPR sensor, aiming to reach a compromise between the low-cost and good sensitivity to the analyte, it is proposed an AuNPs+rGO layer prepared at room temperature using an alternative and eco-friendly method. This production method leaves the nanoparticles capped by polyphenols (ECGC) residuals. The influence of this capping on the LSPR properties of the NPs has been studied by using a computer simulation approach, based on Mie theory and FDTD simulations. The obtained results show that a thin, less than 10 nm, mantle causes a red shift of the LSPR central wavelength toward the 627 nm. The LSPR peak suffers a small reduction, the interaction between the EGCG, the rGO and AuNPs seems to enhance the LSPR wavelength selectivity. This effect will be experimentally validated, as it could represent an important characteristic for this sensing layer.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mlblux.2019.100032.

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