

Plasmonic properties of gold nanospheres coupled to reduced graphene oxide for biosensing applications*

Alessandro Fantoni, Vladan Stojkovic, Miguel Fernandes, Manuela Vieira, Elisabete C.B.A. Alegria, Ana P.C. Ribeiro

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. Reduced Graphene Oxide (rGO) is a type of chemically derived graphene, with equivalent optical properties but easier to be synthesized. This work reports a study about the applicability of rGO as a support for gold nanoparticles (AuNPs). The resulting AuNPs-rGO composites are studied in terms of spectral light transmission and plasmonic resonance as a possible sensing element for a photonic protein sensor device.

INTRODUCTION

Because of its interesting optical, thermal and mechanical properties, graphene has found during the last years its path in a large variety of biosensing applications [1]. Recently, reduced Graphene Oxide (rGO) has been proposed and studied as a nanocomposite in conjunction with gold nanoparticles [2] and also proposed as a biosensing element for aflatoxins [3]. rGO is studied in this work in conjunction with the local surface plasmonic resonance (LSPR) produced by gold nanospheres (AuNPs) and we present results about light transmission and absorption of rGO decorated with AuNPs, evaluating the possibility of using this material as the sensing element for a protein sensor device.

The proposed device structure is depicted in Figure 1. It is a plasmonic structure based on the LSPR interaction of Au nanoparticles, embedded into a matrix of rGO. After proper functionalization with selective antibodies, and for a tuned wavelength, light transmission is controlled by slight changes of the refractive index induced by the biomarker concentration. The use of a functionalized surface based on rGO, allows an improvement of the biocompatibility and a cost reduction. Integration with an a-Si:H photodetector allows the quantification of biomarker fingerprint on the sensing surface. The optoelectronic readout is performed by a pin a-Si:H photodiode. The goal of the work hereby presented is the study of the plasmonic properties of the AuNPs-rGO composites for different light wavelength and nanosphere dimension. The focus of this study is on the LSPR absorption profile, measured by UV-Vis spectroscopic analysis. A theoretical analysis is also presented, based on the Mie theory, about the LSPR of

AuNPs with different dimension, diluted in water and in composition with rGO.

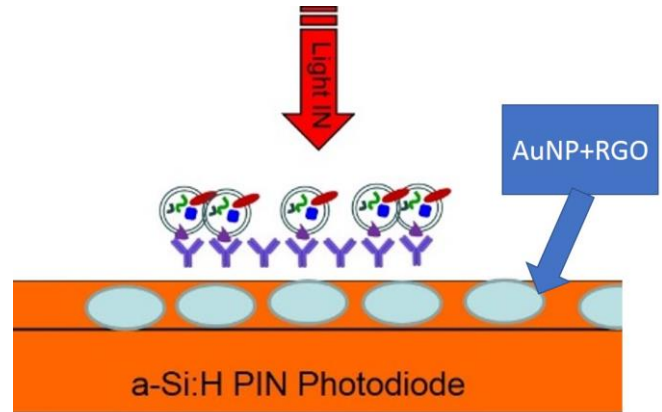


Figure 1. Schematics of the LSPR sensor based on rGO+AuNPS light trasmission properties

I. SIMULATION: MIE ANALYSIS

A. Theory

Even if the plasmonic phenomena were known since the ancient ages, a first theoretical explanation, based on general electromagnetic approach, has been presented only in the beginning of the XX century by Gustave Mie [4]. This theory is still a solid basis for a satisfactory understanding of these phenomena and it is extensively reported [5]. According to the Mie theory, the interaction between light and the nanospheres can be described in terms of the extinction efficiency (Q_{ext}), defined as the ratio of the cross-section for light extinction process, to the geometrical section area of the spherical particle. Light extinction is defined as the sum of the two processes describing light absorption and scattering, introducing the analogue quantities of absorption (Q_{abs}) and scattering (Q_{sca}) efficiency. The Mie theory can be directly applied only to the special case of a spherical particle, admitting an extension to the case of a core-shell sphere. It describes in a very complete way the extinction of a plane

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A. Fantoni is with the CTS-UNINOVA institute, Caparica, Portugal and with ADEETC-ISEL-Instituto Politécnico de Lisboa, Portugal (e-mail: afantoni@deetc.isel.ipl.pt). V. Stojkovic is with ADEETC-ISEL-Instituto

Politécnico de Lisboa, Portugal. M. Fernandes is with the CTS-UNINOVA institute, Caparica, Portugal and with ADEETC-ISEL-Instituto Politécnico de Lisboa, Portugal. M. Vieira is with the CTS-UNINOVA institute, Caparica, Portugal, with DEE-FCT-UNL Caparica, Portugal and with ADEETC-ISEL-Instituto Politécnico de Lisboa, Portugal, E.C.B.A. Alegria is with ADEQ-ISEL-Instituto Politécnico de Lisboa, Portugal and with CQE, Lisbon, Portugal. A.P.C Ribeiro is with CQE, Lisbon, Portugal.

wave without any restriction to the particle size. The Mie analysis requires the values of the complex refractive index (n,k) for the metal and the surrounding medium. Optical properties for metals and dielectrics, necessary for our simulations, have been taken by literature [6,7,8,9].

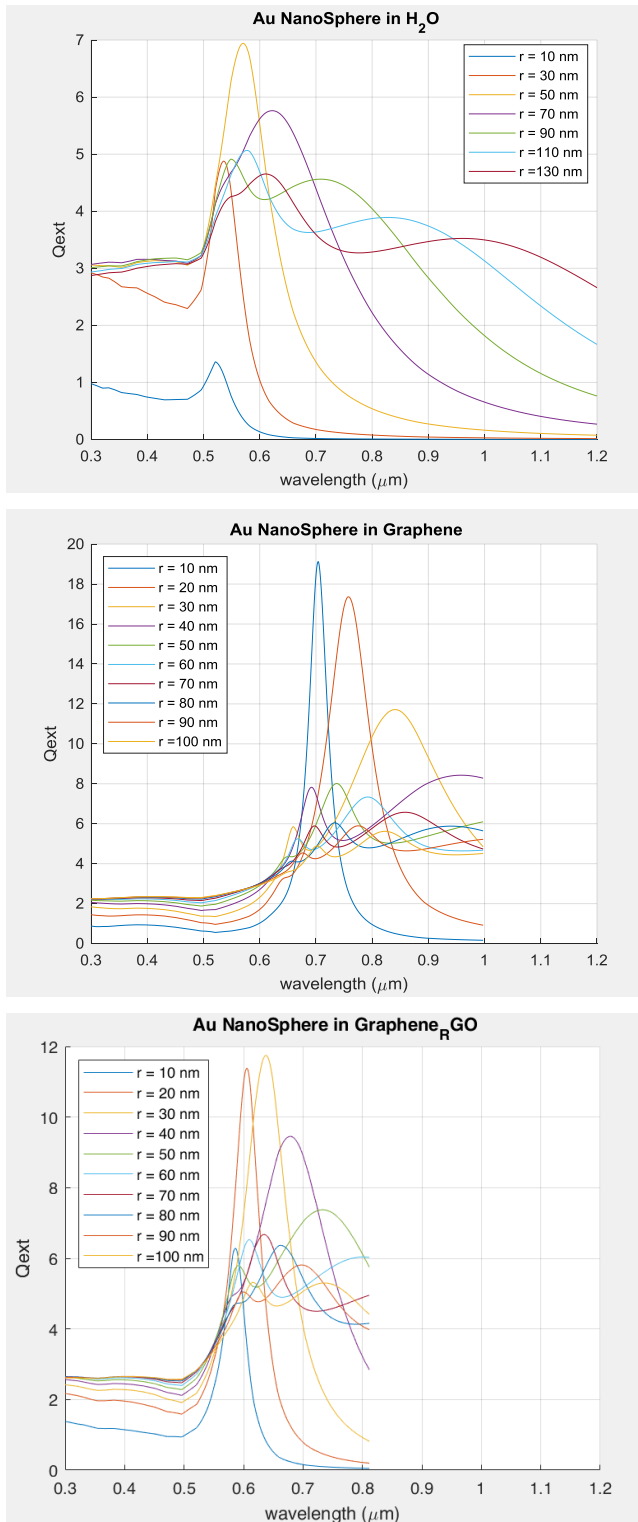


Figure 2. Extinction efficiency, calculated by Mie analysis, for gold nanospheres with radius between 10 and 130 nm embedded in graphene, rGO and diluted in water.

B. Simulations

A Direct Mie analysis has been used to simulate the LSPR of gold nanospheres embedded in Graphene, rGO and, for comparative purpose, in a colloidal solution [10]. As expected, our results show that the wavelength for the LSPR peak depends strongly on the nanoparticle radius. It is also possible to detect an increasing multipolar response and a peak broadening for large sphere radius. On the other hand, a sharp and localized peak can be observed when the NPs radius is small. When the size of the NPs is as small as 20 nm, absorption is the dominant phenomena and the most part of light extinction for these cases is due to the enhance absorption caused by the LSPR. The simulated light extinction for Au nanospheres with a radius in the range 10-130 nm embedded in Graphene, rGO and distilled water is depicted in Figure 2. The resonance peaks wavelength and width vary greatly with the surrounding medium. In rGO the peak is located in the red part of the spectrum, in the 600-700 nm range, depending on the NP size. This result is of greatly importance for our projected applications, as the spectral sensitivity of a-Si:H is still good in this range, becoming much lower when entering in the infrared region (wavelengths above 700 nm). The extinction efficiency of a 40 nm nanosphere covered by a thin layer of rGO with increasing thickness is presented in Figure 3. The rGO cladding layer produces the effect of red-shifting the LSPR peak, proportionally to the cladding thickness.

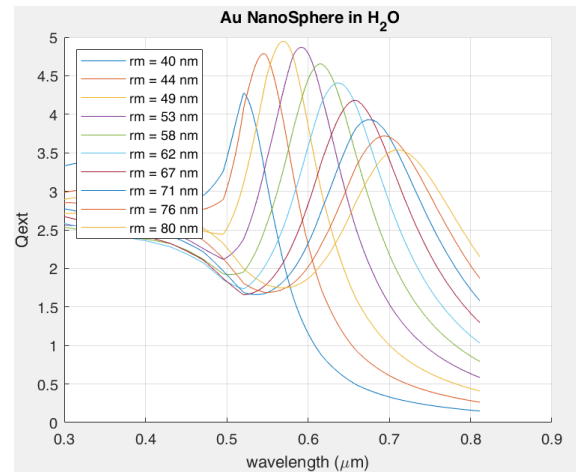


Figure 3. Extinction efficiency, calculated by Mie analysis, for gold nanospheres with 40 nm radius covered by a rGO cladding layer with thickness between 0 and 40 nm diluted in water.

II. EXPERIMENTAL

A Preparation of rGO

A modified Hummer's method [11] was used to synthesize GO, in which graphite powder (1.0 g) is poured into a solution of NaNO_3 (0.5 g) in concentrated H_2SO_4 (30 mL) and cooled to 0 °C. KMnO_4 (3.0 g) is then added, during which the temperature of the mixture was maintained below 20 °C. Successively, the mixture is stirred at 35 °C for 1 h, and then diluted with deionized water (46 mL) by keeping the temperature at 85 °C and then increasing it to 100°C for 30 min. Warm deionized water (140 mL) is then added to the

mixture, followed by the dropwise addition of a 50% aqueous solution of H_2O_2 (15 mL), and the solution is stirred for 30 min. The mixture is then centrifuged and washed with a 5% aqueous solution of HCl (1 L) to remove metal ions, followed by deionized water (1 L) to remove the acid. The dry GO powder is finally obtained after heating the filtrate for 12 h at 60°C . Reduced Graphene Oxide (rGO) is synthesized by a solvothermal method. In a typical synthesis, GO is dispersed into ethylene glycol (60 mL) and sonicated for 1 h, followed by the subsequent addition of aqueous NH_3 (1.6 mL), and stirred again for 1 h. rGO is mixed with AuNPs by ball milling technique. Figure 4 displays the SEM (Scanning Electron Microscopy) image of the produced rGO.

B. Preparation of rGO-AuNPs composite

To prepare the rGO-AuNPs composite, a set of commercially available gold spherical nanoparticles with radius in the 20-50 nm range were used [12]. To achieve a uniform dispersion AuNPs and rGO were mixed through a mechanical process, with a ultrasonic bath at 44 kHz for 15 minutes, and with a sonicator at 20 kHz, for 1 minute. The rGO concentration in the resulting colloidal solutions (3 mL) ranges from 0.5 to 4 mg for solutions containing 5.8×10^{-5} g/mL of gold.

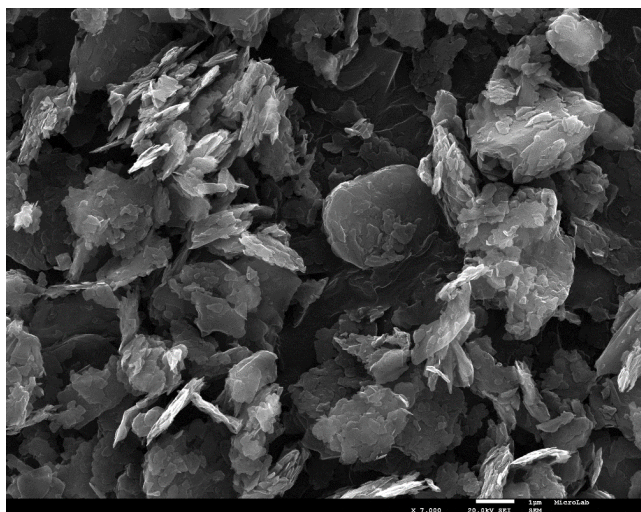


Figure 4. SEM image of the rGO used in the experimental measurements.

C. UV-Vis measurements

Although, no modification in the LSPR wavelength was detected for nanoparticles with radius less than 40 nm, the influence of the rGO coupling to AuNPs could be clearly observed for 50 nm radius nanoparticles. Figure 5 shows the light absorption profile in the visible range, for different concentrations of rGO. The presence of rGO results in a general reduction of light transmission over the entire spectrum, in comparison to the solutions containing exclusively AuNPs. The LSPR peak, to be ascribed to the plasmonic behavior of the nanospheres is well defined in all the measured cases. The central wavelength for this plasmonic resonance is red shifted by the AuNP-rGO coupling, as reported in Figures 5 and 6, where the peak

wavelength is plotted as a function of the rGO concentration. This is in accordance with the simulation results described in Figures 2 and 3. Comparing the simulation and the experimental results we can conclude that even if there is no complete covering of the AuNP by the rGO (that is the cladding has by no means a uniform thickness, as simplistically assumed in the Mie analysis) the plasmonic resonance wavelength is affected by the difference in the refractive index introduced by the rGO. If no rGO is introduced, the observed LSPR is almost in perfect agreement with the simulated data. The red shifting caused by the increasing rGO concentration can be ascribed to a better and more complete cladding of the nanoparticles. It should be noted that the resonance peak remains unique and we cannot observe superposition of two separate peaks related to the cladded or not-cladded NPs.

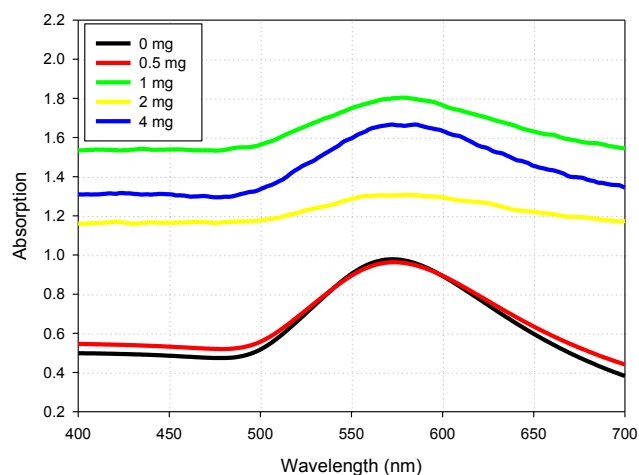


Figure 5. Measured absorption profile of the rGO+AuNP colloidal solution with different concentration of rGO

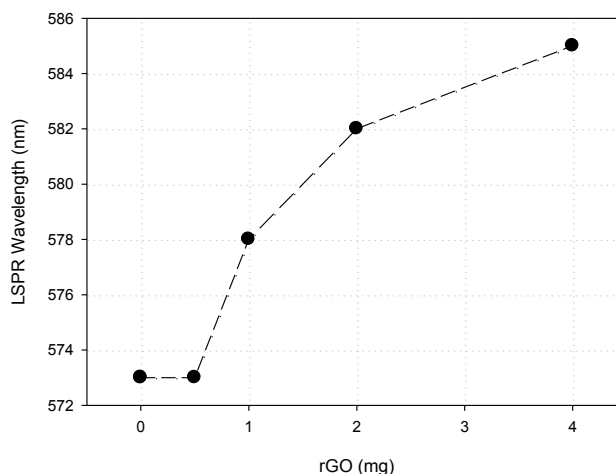


Figure 6. LSPR wavelength measured by UV-VIS absorption of rGO+AuNP colloidal solution, as a function of the rGO concentration. Nanoparticle radius is 50 nm.

III. CONCLUSION

Considering that the AuNP-RGO composite is a promising candidate as a support for antibodies functionalization as the sensing layer if a photonic biosensor, we have demonstrated that it is possible to obtain a uniform mixture of AuNP and rGO using mechanical process like ultrasonic bath or ultrasonic sonication. Anyway, when the AuNP diameter is smaller than 100 nm no modification of the LSPR response can be observed. For 100 nm AuNP the mixture with rGO

cause a red shift of the LSPR and the red shift depends on the RGO concentration. On the way for a biosensor application, future work will focus on an efficient method for functionalization with antibodies and the deposition of the composite on top of a photodiode photo-active surface.

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