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Enhanced Gold Nanoparticle Optics for Nanophotonics, Photovoltaics and Green Photonics Insights

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Abstract

In this communication it was developed the basis of Nanotechnology and fundamental Research focused on Nanophotonics and Green Photonics for Biophotonics and Implantable devices with varied interest and applications. Thus, gold Nanoparticles as Optical active Nanomaterials presented different advantages in comparison to other materials due to their biocompatibility, low toxicity depending of chemistry of surfaces, and capability to generate high Electromagnetic fields known as Plasmonics properties. In addition gold Nano-surfaces are relatively easy to be conjugated with other materials due to their soft electronic bonding and polarizable surfaces. These characteristics provide to gold Nanoparticles interesting insights and future perspectives within Nanophotonics and Green Photonics developments. Thus, Nanophotonics based on gold Nanomaterials provide excellent light matter interactions accompanied with the generation of varied quantum and non-classical light properties. In this context, it should be noted recent trends of Green Photonics where materials and associated properties should be biocompatible contemplating their fabrication too. It is a great challenge to develop Green Nanomaterials with Enhanced conductive and luminescent properties; however gold based Nanomaterials are showing interesting insights within Nanotechnology. In these perspectives and looking for new Optical active materials it should be highlighted the design and fabrication of devices from the Nanoscale and beyond. And, it should be highlighted the particular interest on Implantable Optical active devices due to their potential perspectives within Life Sciences. Therefore, in this short Review it was intended to afford to discuss about how gold Nanomaterials could provide insights within Nanophotonics, Green Photonics, and Life Science applications.

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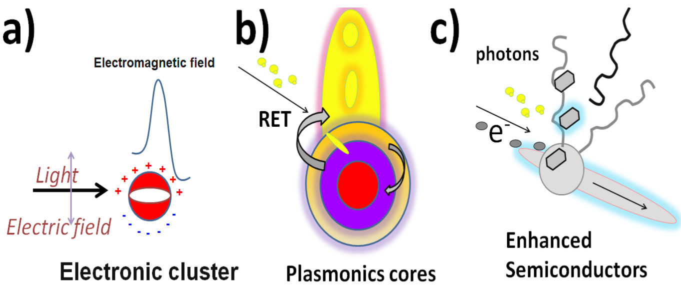
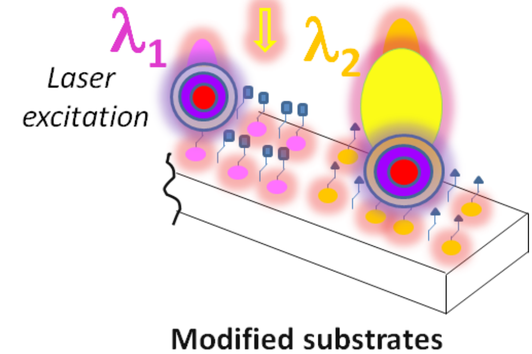
Introduction

Gold Nanoparticles as noble metal [1] showed very interesting characteristics to design Hybrid Nanomaterials [2]. This versatility joined to other materials permitted to design varied types of Nanoparticles modified with different chemical modifications [3]. Thus, it was afforded to different properties. In this regard it should be noted the particular electronic configuration that permits to interact with its surrounding media permitting to link different types of Chemistries and related strategies. In addition, it should be highlighted the capability to produce high intense electromagnetic fields known as Plasmonics [4]. So, gold Nanoparticles could provide a platform with tuneable optical active properties by joining other materials [5]. In this regard it is highlighted gold Core-shell Nanoparticles due to their Nanoarchitecture that permit their tuning by different material incorporations [6] **(Scheme 1)**. Thus, by an appropriate excitation it could be developed varied photonics processes within the different materials as well coupling to transfer energy modes through space and time [7]. This is the case of Plasmonics properties **(Scheme 1.i)** that produce high electromagnetic fields varying the intensities based on the metal involucred. In similar manner Multi-layered gold Core-shell Nanoparticles could develop Reaction Electron Transfers (RET) within different membranes; and produce Metal Enhanced Fluorescence (MEF) [8] **(Scheme 1.ii)**. In similar manner Electromagnetic fields within the Nanoscale could affect electronic phenomena from the Near field towards the Far field [9] **(Scheme 1.iii)**.



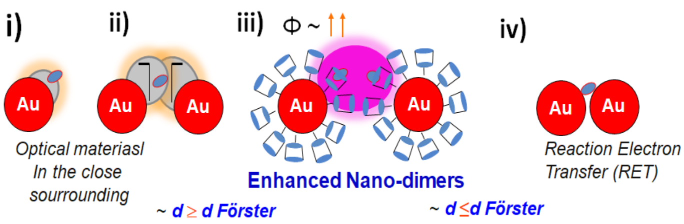
Scheme 1: Schema of Optical phenomena from Nano-sized platforms. **(a)** Gold Nanoparticles with representation of the electronic surface and Electromagnetic field generation; **(b)** Multi-layered Core-shell Nanoparticle with the generation of varied Energy transfers; **(c)** Representation of the Enhanced electronic conduction in presence of Electromagnetic fields generated in the Nanoscale. Reprinted with permission of the author A. G. Bracamonte et al. Copyright 2023.

This is just considering the confined Nanoscale; however towards further distances could be extended the energy transfer. In this context, it could be noted the design and synthesis of Plasmonic Resonant waveguides from it is possible to enhance excited varied Energy modes [10]. It is a current high impact Research field that it is currently in progress that should be known in order to propose new Optical Set ups based on the incorporation of accurate controlled Optical active Nanoplatforms. As for example it could be proposed modified substrates with Smart Optical Nanoplatforms [11] that in presence of targeted Biostructures or Biomolecules could act as Chips for Biophotonics and early diagnosis applications **(Scheme 2)**. In these prototypes could be developed non-classical light and other recognition strategies to detect molecules, Biomolecules, and Biostructures.



Scheme 2: Modified substrates to prototype smart Chip surfaces with Smart Optical Nano-patterned surfaces to develop varied physical and chemical phenomena such as non-classical light and other recognition strategies to detect molecules, Biomolecules, and Biostructures. Reprinted with permission of the author A. G. Bracamonte et al. Copyright 2023.

In this context, Green Photonics recently showed interesting perspectives within materials for Energy applications such as light harvesting, and further applications towards miniaturized devices and instrumentations [12] where Green principles [13] should be considered due to environmental and Biological implications [14,15]. In these perspectives, gold Nanoparticles could act as a Biocompatible material that could be in direct contact with cells and Biological tissues. And it could afford to enhanced Plasmonics properties by an appropriate Nano-array to couple different high electromagnetic fields from the individual Nanoparticles to resonant collective collection of particles [16]. It could be mentioned that by a proper chemical modification it could be tuned interaction between Nanoparticles and inter-Nanoparticles spacers increasing Plasmonics properties and generation in their close and longer surrounding improved and enhanced physical phenomena such as Enhanced Plasmonics coupling with Metal Enhanced Fluorescence [17] (**Scheme 3**). In these perspectives, simplifying variables and focusing on distances of interactions of it could be mentioned that close interactions could produce partial increases (**Scheme 3.i**); while optimizing distances and chemical modifications to place the Optical active material in the highest Electromagnetic field produced by individual Plasmonic Nanoparticles and Enhanced Plasmonics (EP) dimeric species as well, it could be developed Enhanced properties (**Scheme 3.ii, and iii**). However, the Optical active material if it is adsorbed on Nano-surfaces suffer quenching by Electron Transfer Reaction (RET) towards the Nanoparticle (**Scheme 3**.iv).



Scheme 3: Scheme of gold Nanoplatforms interacting with Optical active material in their near sourrounding: i) single gold Core interaction in the close surrounding; ii) Dimers interacting with their respective Electromagnetic fields within the near field contemplating distances between them (d) higher than the Forster distance (d Forster); Enhanced interactions between two modified Nanoparticles to incorporate Optical active molecules; iv) adsorbed Optical materials on gold Nano-surfaces that generate Electron Transfer Reactions (RET). Reprinted with permissions of A. G. Bracamonte et al. 2022.

Therefore, focusing light on Nanoparticle property tuned it could be developed Nano-Optics for targeted applications and studies. In order to do that, it should be incorporated the Optical active Nanoplatforms within an Optical Set Up, from where it could be developed the best conditions and desired properties [18]. Thus, in this brief Review it was discussed how it could be tuned gold Nanoparticles as well as other Nanomaterials by a proper Optical set up applications. So, by joining Optics from different levels could be afforded to Enhanced Nano-Optics and miniaturized Optical instrumentation [19].

Development of Optics and Nano-Optics

This introduction intends to explain and discuss how Optics in the macroscale was developed towards de micro-scale towards smaller resolution [20,21]. Optical instrumentation permitted to manage light and electronic properties in order to create varied signalling, imaging, and new modes of energy that could be applied as well to the next generation of instrumentation. And, there it is where it is of interest the development of new materials to support Optical components and Optical actives substrates. In this direction, it was confined the limits of the discussion looking for developments from chemistry and physics to design materials to develop Optics. In this manner, the development of Optics are related with accurate Optical elements positioned on specific benches where distances should be controlled [22]. It is necessary to incorporate light sources aligned with sample support where the system of study is focused. Moreover, in the middle many Optical lens and mirrors should be participating in the signal transference and transduction. In this light pathway the signal could be modified, amplified, enhanced depending of the prepared Optical set up prepared [23]. This brief description from the macroscale with visible optimal components, it should be a model to develop Optics within smaller dimensions. So, it is know that reducing sizes of Optical instrumentation afforded to challenges related with limitations of Physics and availability of Optical components

In these perspectives, to generate new Optical active materials it was begun to develop the idea of Nano-Optics focusing light within confined and controlled Nanoarchitectures [24]. Thus, as reference of the system of study and challenges related, for example it could be mentioned that a standard laser beam could focus light with high power of irradiance within the micro-scale dimension in close relation with 1 micro-meter. This mention is to have an idea about the capability of standard advanced instrumentation such as Lasers to focus on surfaces and volumes where is possible to contain few number Optical active Nanoarchitectures. And, by this way depending of the intrinsic material constituents , it will be the response achieved, Thus, the design and fabrication of Optical Nanoplatforms could be afforded as particular Optical active Nanostructure with key elements and molecular constitution that permits the development of varied modes of energy and non-classical light as well as quantum phenomena [25]. But, at the same time the Nanoarchitecture could play a role as Optical active platforms; where in general the Nano-surface is modified with other molecules, elements, functional materials [26].

So, most know Nano-Optical shapes are spherical could irradiate varied coloured non-classical light from single Nanoplatforms; however these Nanoarchitectures could be joined to other ones by molecular shuttle, molecular linkers, biomolecules, etc. ; and by this manner obtain assemblies with modified Optical properties **(Figure 1)**[27]. As for example, supramolecular Nanoparticles grafted with Laser dyes interacted and formed variable sizes of Nanoaggregates, that depending of the state of development of them, it was the effect obtained on the fluorescence emission. Thus, Nanoaggregates sizes below 500 nm, due to the short distances of the molecular spacers produced quenched emissions of the guest **(Figure 1a)**.; while higher Nanoaggregates it was measured an enhanced fluorescence emission effect based on EP and MEF **(Figure 1b)**. It should be mentioned that the Supramolecular system used was cyclic-oligosaccharide macrocycle with seven unities nominated as β-Cyclodextrin (βCD) [28]. It forms host guest complexes with many Laser dyes and interact strongly between them that produced Nanoaggregates.

In this manner, it could be noted that the modified optical properties are generated from many parameters and factors to control such as; i) the intrinsic material composition; ii) shapes; iii) spacer lengths; iv) Nanoaggregation; Nano-assembly formation; v) media; vi) physical properties involucred; vii) variables and phenomena associated such as refractive index, light scattering properties, electronic bands, electronic binding, and consequent new phenomena generated as high energy electromagnetic fields and Plasmonics. Moreover, the incorporation of these Nanomaterials within reduced sized substrates permit focus light within well-defined spaces that contribute as well to the generation of new modes of energy and resonant propagation through space and time. This basic concept could represent waveguides and micro-device substrates where light or electrons are conducted through the material. In similar manner, this is the basic concept of other Opto-active materials from where molecules and Nanoparticles switch on/off targeted functions [29]. In this manner it was presented and discussed the main considerations to have into account Nanoptics with perspectives to Nanotechnology towards miniaturized Instrumentation as well as standard Optical Instruments.

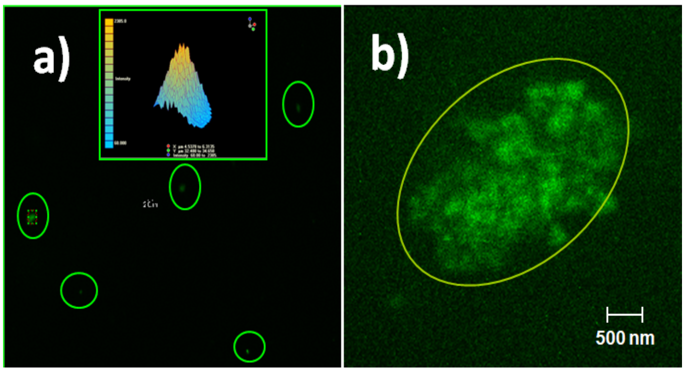


Figure 1: Fluorescence microscopy of Rhodamine B complexed with gold Nanoparticles βCyclodextrins (βCD) grafted with 1,3-propanedithiol: **(a)** small size aggregates. Image inlet: Representative 3D surface emission graph for both Nanoparticles samples where it is shown the emission of each fluorescent nanoparticle hot spot. **(b)** higher size aggregates. Reprinted with permission from Ref 27 (A. G. Bracamonte et al.). Copyright 2019 Microchemical Journal, Elsevier.

Nanophotonics and Green Photonics

In the way to develop Nano-Optics controlling the Nanoscale and generating Nanophotonics properties with targeted functions such as energy collection and harvesting [30], it could be noted the importance of photons and light matter interactions [31] that amplify absorptions, harvesting, and signalling depending of the particular need [32]. Thus, in this brief section it is intended to highlight new trends and needs from real applications from the market in close relation with fundamental Research that it is embedded to provide optimal results beyond the Nanoscale [33]. And, in this context, Nanophotonics is involucred in many Research fields; however it of high impact and interest to show in this case, the developments towards clean energies and materials [34]. Green Nanophotonics could be defined as the study and development of applied Optical systems focused on renewable energy; where it is associated to photovoltaic devices, Light emitter devices, light emitter displays, and all related Opto-electronic devices [35]. So, the vision is wide and compromise that all the development should be eco-friendly with long term objectives [36]. Thus, performances and Biocompatible materials appeared to be challenges that Nanophotonics could afford and improve.

Hence photons are delivered controlled and could be counted, the developments of new Nanophotonics materials are accurate with high sensitivity against little media modifications [37]. Thus; success in the improvement of improved performances of energy harvesting and transfer could be considered as not so high for neophytes; but it involucred many optimizations in different parts of hybrid hetero-junctions as for example. In this manner, with the pas of time efficiencies are improved and functions too [38].

Optical active Nanoplatforms design and synthesis are highly required and it is intended to even improve more current state of the art. So, gold Nanoparticles could afford to Biocompatible Nanophotonics materials. But, depending of the targeted function there are other semiconductors that could be incorporated to participate within enhanced or improved photonics processes [39,40]. As well other Carbon based compounds are highlighted such as Graphene and derivatives[41].

For example It could be mentioned optical active metamaterials with different applications for opto-electronics, micro-, and nano-circuits [42] with low energy application are required for stimulation [43]. This challenge could be afforded by different strategies and manners, but in order to show how it could be improved Opto-electronics by joining different Nano-Optics and semi-conductive properties, it is mentioned heterojunctions [44]. Thus, it is known for optimal efficiencies of perovskite solar cells (PSCs), it should be diminished energy losses produced by different mechanism such as interfacial defects [45]. Looking for significant improvements, it was designed a rubidium-doped triple cation–based perovskite [e.g., Rb-doped Cs0.06FA0.79MA0.15Pb(I0.85 Br0.15)3] incorporated in a multilayered device with varied nanomaterials [46]. First, an evaporated dopant-free tetracene (120 nm) on top of the perovskite layer, capped with a lithium-doped Spiro-OMeTAD layer (200 nm) and top gold electrode permitted a minimal interfacial defect. By this manner, the photoluminescence perovskite layer interfaced between these graded hole transport layer (HTL) and a mesoporous TiO2 electron-extracting layer, reached to 15% in comparison to 5% for the perovskite layer interfaced between TiO2 and a Spiro-OMeTAD alone. Therefore, it was demonstrated an efficiency up to 21.6% accompanied with an extended power output of over 550 hours of continuous illumination **(Figure 2)**.

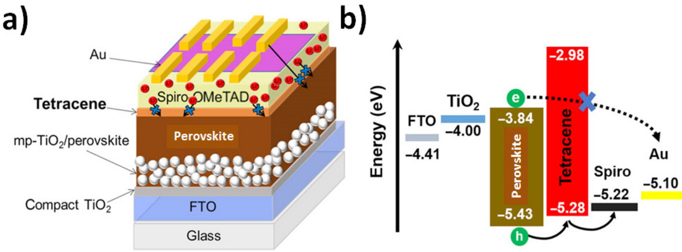


Figure 2: Solar cell architecture and energy diagram. **(a)** A device architecture schematic and, **(b)** energy-level diagram obtained from UPS measurements of a complete solar cell with graded doped HTLs of undoped tetracene with a doped Spiro layer. In the schematic, the red spheres are representative of Li+ ionic dopants present in doped Spiro layer, and the short and long arrows demonstrate the extrinsic ionic and Au migrations that are blocked by the undoped tetracene layer. The perovskite composition is Rb-passivated Cs0.06FA0.79MA0.15Pb(I0.85 Br0.15)3. Reprinted with permission from Ref 46 (R. H. Friend et al.). Copyright 2019 Science Advances, Science.

Thus, as it could be observed the proper incorporation of varied Nanomaterials within hetero-junctions provided interesting Photovoltaic improvements. In this context it should be noted that individual Optical properties afforded to coupling different physical phenomena where electrons where involucred and passing through to finally target the desired function.

Conclusions and Future perspectives

In this manner it was intended to introduce knowledge from how Nano-Optical properties of gold as well as other semiconductors could be incorporated in other types of studies and Research fields such as Nanophotonics, Photovoltaics, and new trends of Green Photonics. Then, fundamental Research focused on single Nanoparticles with Nanophotonics techniques and methodologies associated with special Optical Set ups showed insights and real applications within Optical active materials such as for Photovoltaics and Solar Energy cells uses. In this context, it was noted that from single Nanoparticles were afforded different properties in comparison to collective Nanoparticles associations within hetero-junctions and Luminescent materials. In addition, it was noted that Enhanced phenomena based on Electromagnetic fields coupling with other Opto-electronic materials could improve final properties in the far field applications. Thus, considering by this manner the near field within short Nanoscale lengths as important factor to control and study, it should be highlighted developments in these intervals of sizes. Therefore, future perspectives are being shown within reduced sizes of Optical active Nanomaterials in close relation with Quantum levels. By this manner, new concepts and proofs of concepts are being incorporated or considered such as Nanolasers and Quantum cascade Lasers. In these developments are involucred varied coupling physical and chemical phenomena to enhance final properties. So, the next generation of Metamaterials and Enhanced Nanomaterials are in progress in the cutting edge of the state of the art in the design of new Nanoarchitectures and material prototyping. Then, it is expected the development of modified substrates to transfer varied Energy modes through space and time too. In this context, considering special needs for Biocompatible applications such as for Biophotonics and Green Photonics, it is expected gold based Nanomaterials as important component within complex Optical active materials.

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