

## REVIEW

# Nano-Engineering Versatile Core-Shell Nanoplatfoms for Tuning Enhanced Opto-electronic Matter Interactions

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**Abstract:** In this communication, it is presented the concept of optics based on Core-shell architectures controlling the nanoscale and beyond. It is demonstrated how these types of architectures can be designed, from prototyping to synthesis, using colloidal and laser-based techniques. This particular nanoarchitecture was presented as a fundamental structure that can be tuned as needed through the use of various materials, enabling control over size, shape, and topological features. Then, the impact of Core-shell nanoarchitecture to tune photon and electron matter interactions to enhance physics and chemistry with perspectives of non-classical light generation is shown. Therefore, fundamental wet chemistry to advanced nano-optics studies by the use of Core-shell nanoplatfoms is discussed. In this regard, varied phenomena such as enhanced and amplified approaches are presented. Enhanced based techniques such as metal-enhanced fluorescence (MEF), phosphorescence (MEP), enhanced quantum phenomena (EQ), and amplified signaling are of interest. In this context, the control of nanoarchitecture should be accurately controlled to place the different optical components. Optical active materials are varied to tune photon matter interactions accompanied by the generation of new modes of energies. These emerging non-classical light pathways involve strong electromagnetic field interactions, which significantly influence the electronic and optical properties of all participating materials. Moreover, photonics pathways could be modified to stabilize the excited state, increase quantum yields, and improve performances. In this context, the tuning of high-intense electromagnetic fields related with plasmonics and pseudo-electromagnetics from other semiconductors such as carbon-based materials was presented. Thus, targeted enhanced nano-emitters are presented and highlighted in this article; however, further discussion towards enhanced optics is discussed. In this manner, highlights from the nanoscale to far-field optical studies and applications are opened. So, Core-shell nanoarchitectures are presented as important optical nanoplatfoms with high impact within varied optical set-ups.

**Keywords:** optical active nanoplatfoms, Core-shell nanoparticles, nano-optics, confined light, enhanced emissions, amplified physical phenomena, non-classical light

## 1. Introduction of Core-shell Architecture for Nano-Optical Platforms and Further Cargo Loaded Based Technology

Optical materials are composed of diverse matter compositions, and their intended applications or uses depend on these specific compositions. Thus, the application can be regarded as both a fundamental study and an applied development in many cases, since the generation of optical and nano-optical materials is closely linked to real-life optical phenomena—such as smart glasses [1], devices, and other widely used and increasingly adopted wearables [2]. These mentions are noted as the importance of these components is vital to tune optical properties

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where the nanoscale [3] could assume important functions. Therefore, different materials can be developed—or entirely new ones, such as metamaterials—by combining various properties within confined volumes or solid matter [4]. The generation of alloys could produce new properties, functions, and targeted applications [5]. However, the design and synthesis within the nanoscale combining different layers and shells could produce confined matter with potential nano-metamaterial production and further potential properties considering inter-layer interactions. It means that from the whole a different property in comparison to free components is produced. Only in this way can the high impact of nano-optical platforms for the next generation of nanotechnology be achieved. However, other strategies could be proposed to confine matter with opto-electronic and quantum properties accurately deposited by incorporation of different and concentric shells [6]. The growth of multilayered nanomaterials could be based on solid core templates in order to obtain the Core-shell Nanoarchitectures within

different interval of sizes in the nanoscale [7], as well as below and close to the quantum level [8]. This concept could be easily designed and understood from a basic scheme where spherical and well-shaped core templates are covered by concentric additional materials. In this manner, properties from the core could be conserved upon needs and tuned the second layer controlling their compositions towards longer lengths (Figure 1(a)). This is the basic Core-shell structure that could develop varied optical phenomena. In this regard, there are many research works in progress and not all phenomena are under focus. So, it is another optical set-up to consider for further developments towards opto-electronics and quantum phenomena as example.

In this context, it is important to highlight the capability to generate strong electromagnetic fields within the near surroundings at the nanometer scale, from which many enhanced phenomena arise. These mentioned phenomena could be explained by different radiative pathways by the interaction of the fluorophore placed at an optimal distance to receive a high-intense electromagnetic field generated by the electronic oscillation of the metallic core: (a) by an enhanced absorption, (b) augmented excitation of the fluorophores accompanied by increased emission; (c) enhanced radiative decays accompanied, and (d) diminished non-radiative decays. Depending on the fluorophores and nanoarchitectures, the radiative pathways involved may vary; however, in the presence of metal-enhanced fluorescence (MEF) effects, the enhanced fluorescence emissions are accompanied by a shortening of fluorescence lifetime decays [9]. The enhancement factor depends on many variables such as metal core used, shapes, sizes and 3D dimensions [10], intensity of the electromagnetic field generated [11], degree of fluorophore-plasmon coupling, and quantum yields [12]. So, in order to tune luminescence properties, many variables should be taken into account. And, Core-shell nanoarchitectures formed by a metallic Core template covered with modified optical transparent polymeric silica shells with fluorophores permitted an accurate control of many of the main mentioned variables that affect this phenomenon.

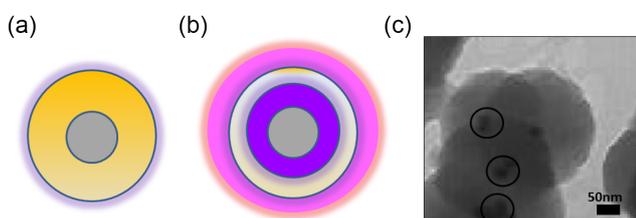
Moreover, multilayered approaches could be designed incorporating varied materials associated with different optical

active properties to tune new nano-optical phenomena. Thus, from the core and passing through different materials electron and photons produce opto-electronics and photonics responses of fundamental and applied interest (Figure 1(b)). Both conceptual designs can be translated to the laboratory bench to produce, for example, silver nano-core templates coated with multilayered polymeric shells. The silver cores in this case provide strong plasmonic properties that could affect electromagnetically the near surrounding to the far-field as well, while the modified polymeric shells could be formed by different materials that act with varied functions. Thus, in brief the core is a high electromagnetic field emitter accompanied by multi-polymeric layers used as support as well as optical active substrate (Figure 1(c)).

Based on these nanostructures, a high versatility was demonstrated, exhibiting optical properties not previously observed in molecules, colloids, or solid substrates. Thus, the use of metal nanoparticles has led to the development of well-defined and time-stable Core-shell nanoparticles. The generation of ultraluminescent nano-emitters exploiting plasmonic enhancements was highlighted. This advancement was enabled by the ability to incorporate various types of materials within different layers, allowing for the tuning of final emissions. In this regard, from literature the translation from the nanotechnology to biotechnology using enhanced phenomena based on electromagnetic fields-matter interactions is noted [13]. The design process involves multiple research fields, such as computational modeling of electromagnetic fields and homogeneous fabrication techniques, which together enable predictable and controllable MEF [14] paving the way for broader applications in other research areas where the electronic densities of materials may be affected. Examples of these include quantum phenomena, semiconductor band structures, molecular orbitals, and electronic densities across various substrates. The Core-shells, in these cases, act as high-intense energy sources affecting their close surrounding with potential applications towards longer distances over time. In this context, electronics and energy transfers could overcome the near fields by the right tuning of optical set-ups controlling nano-optics-based phenomena from single nanoarchitectures to assemblies and nano-arrays. In this way, light propagation through waveguides [15] can be tuned, having a significant impact on nano- and micro-devices, chips, lab-on-a-chip systems, and miniaturized instrumentation [16]. Moreover, the capability to modify solid substrates affected the technology where multilayered approaches are used such as heterojunctions [17], light emitting devices (LEDs) [18], and solar cells [19]. The Core-shells act as photovoltaic nanometer scale cells embedded in photo-cross linkable organic semiconductors [20]. This modification increases total surface of contact and it improves exchange of energy in their inter-phases. In this way, the nanoarchitecture enhances phenomena involving electron densities. Their incorporations resulted in higher performances in comparison to non-modified substrates. Thus, an improved large-scale integration due to the capability to manufacture these nanomaterials by different techniques and methods is highlighted [21]. Therefore, the nanotechnology [22] towards a device miniaturization and the development of new reduced sized optical instrumentation is more easily transferred [23].

**Figure 1**

**Core-shell nanoarchitectures: (a) Schema of core template surrounded with a different material shell. The gray core represents silver nano-template for example. (b) Schema of multilayered Core-shell nanostructures with varied material incorporation. The gray metallic nano-template is surrounded by multi-colored shells. Each color represents different luminescent dyes incorporated within polymeric shells. (c) Transmission electron microscopy (TEM) of tiny silver core templates covered with multilayered polymeric shells incorporating different optical responsive materials. The metallic core template shows a higher electron density, while the multilayered structures are not visible but they are optically active up on laser excitation. And the order and localization of the different shells have an important impact on the non-classical light generated and optical properties**



## 2. Design and Synthesis of Core-shell Nanoarchitectures

As it was introduced in the previous section, the concept of Core-shells in the design of nanoarchitectures affords the tuning of optical properties from the molecular level to the nano-, micro-, and macroscale. This nanoarchitecture is noted as a strategy for providing

hierarchically organized, cargo-loaded symmetrical and asymmetrical confined matter [24]. This fact is the key factor to control looking for the development of new nano-matter properties or applications. Thus, it is important to mention that different types of Core-shell structures reported in literature as well as insights of new ones are presented for further discussion accompanied by their correspondent highlights of synthetic methods [25]. From these capabilities, the intrinsic versatility of the nanoarchitecture and properties as well is generated.

## 2.1. Strategies of synthesis to control Core-shell nanoarchitectures

The following classifications and descriptions are based on the complexity and matter constitution of the nanoarchitecture. The Core-shells are mainly spherical, but the control of sizes and shapes as well could be afforded in the last subsection due to its importance. Initially, polymeric reactions enabled the synthesis of multilayered polymeric Core-shell structures, which were later modified by incorporating nanoparticles of other materials as templates. After that, the Core nanostructures could be modified with mono- and multilayered molecular and short polymeric chains affording to modified cores with stabilizing branches with variable sizes.

Then, it is presented the modification or combination of different nanoparticles to achieve cores decorated with surrounding nanomaterials from different sources. In this manner, the second layer could be formed by inorganic, organic, and bio-nanomaterials. In all the previous approaches, the importance of covalent and non-covalent linking takes an important role in their formation and stability. Finally, bimetallic and further inorganic joints are shown highlighting other synthetic pathways such as based on oxidation/reduction reactions and electrochemistry [26].

In this manner, different electronic, quantum, and optical properties could be combined managing different chemical reactions and strategies based on Core-shells that could tune further sizes and shapes as well [27]. The sizes are very important to control due it could be tuned from quantum phenomena close to 1–2 nm, while higher size nanostructures such as below 500 nm could afford to tiny opto-electronic surfaces acting as optical active nanostructures. Thus, molecules could affect the quantum scale and properties related, while higher sized could be considered as potential smart optical active nanostructures towards nano-devices. However, intermediate sizes considering the full nanoscale control could vary properties and chemical synthetic pathways. This mention is

related as for example to use tiny sizes with strong Wanders-Walls interactions to induce adsorptions and spontaneous assembling [28]. This fact summed to additional covalent and non-covalent reactions could produce improved reactions and targeted Core-shell nanoarchitectures [29]. The following sections present a range of strategies, from the most well-known to emerging ones, accompanied by advanced concepts. In the current status of the art focusing on the capability to design different Core-shell architectures was highlighted.

## 3. Strategies to Generate Versatile Core-shell Nanoarchitectures

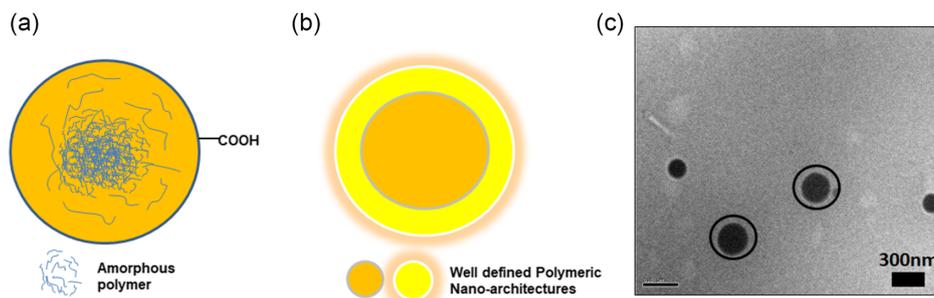
### 3.1. Polymeric Core-shell nanoparticles

The Core-shell nanoparticles could be developed by polymeric reactions tuning from monomers to additional optical active materials as well as further functional structures [30]. Polymers permitted to control chemical structures from single molecules to higher sizes (Figure 2(a)). Moreover, polymerizations are influenced by the media, surfaces, and additional interactions, alongside inter-monomeric linking and crosslinking interactions [31]. In this regard, the Cores could be contemplated as well to be formed by inorganic and organic polymeric nanostructures [32]. So, from spherical polymeric architectures the next polymerization reaction in order to confine cores acting as templates by the second polymeric net could be modified [33]. In this particular bottom-up approach, the use of various biodegradable monomers was highlighted, forming three types of multilayered shells with unique characteristics from different perspectives. Thus, two types of polyelectrolyte shell composed of biocompatible and biodegradable polyelectrolytes poly-L-lysine hydrobromide (PLL), fluorescently-labeled poly-L-lysine (PLL-ROD), poly-L-glutamic acid sodium salt (PGA) and pegylated-PGA (PGA-g-PEG), and hybrid shell composed of PLL, PGA, and SPIONs (superparamagnetic iron oxide nanoparticles) were incorporated. Therefore, multilayer shells were constructed by the saturation technique of the layer-by-layer (LbL) method. These types of nanoparticles could be decorated with other quantum and plasmonic materials with interesting perspectives towards biolabeling, biophotonics studies, and bioimaging uses.

This capability could afford the basic Core-shell proof of concept towards the development of new polymeric approaches, structures, etc., highlighting the polymer as the vital molecular structure incorporation in all cases (Figure 2(b)). In this regard, this communication is not

Figure 2

**Polymeric Core-shell nanoparticles formed by (a) amorphous polymeric gel or porous nanostructures surrounded by a full polymeric coverage. The lines represent amorphous polymeric chains that could be cross-linked or not, as well as generating porous polymeric materials. (b) Core-shell polymeric structure formed by a well-defined and solid core surrounded by a second polymeric shell. Therefore, Core-shell structures formed by two different polymeric materials afforded to versatile chemical structures with potential uses as optical active platforms within the nanoscale. (c) Real polymeric nanoparticles overloaded with laser dyes. The definition of the polymeric particle, size and shape depends on the polymer involved and media where the polymerization is achieved**



intended to classify all the types of polymeric reactions and polymers existing actually in literature; however, it is of interest to open the discussion towards the design of new polymeric structures formed by covalent, non-covalent interactions, and hybrid structures [34]. In this regard, there are so many approaches from substrate developments, none transferred yet into the nanoscale. As for example, multilayered approaches actually used from technology such as energy generation and light production via different sources of stimulations and energy modes passing through are excellent sources of inspirations to develop new Core-shell nanomaterials within the Nanoscale [35]. This approach does not aim to simply reduce macroscale materials to smaller sizes, but rather to confine and control the composition of matter in order to study enhanced pathways, signal amplification, quantum phenomena, and other related effects.

In this context, phenomena ranging from enhanced fluorescence resonance energy transfer (FRET) [36] to the amplification of nanolaser signaling are noteworthy. Additionally, ongoing research in silicon photonics is paving the way for precise control at the nanoscale, particularly in silica-based materials. Silica nanoparticles (Figure 2(c)) demonstrate promising potential, offering intriguing perspectives from chemistry to nano-optics as optically active substrates [37].

In order to conclude this subsection, polymers from different sources could afford to tunable soft matter constitution [38] with relative easily combination with a broad spectra of optical active materials from molecules to inorganic materials. In this way, it was possible to generate both well-established polymeric structures and new ones, while also contributing to ongoing research across various length scales.

### 3.2. Synthesis with nano-templates

Core-shell nanoparticles could be templated by well-defined and solid metallic nanoparticles such as from noble metals, semiconductors, and quantum materials. As introduced, modifying synthetic polymeric reactions through the incorporation of nanoparticles and colloidal stabilizers can induce the initiation of polymerization reactions on nanosurfaces. In this regard, it should be noted that the interaction between monomers and chemical agents as stabilizers on surfaces should fit by non-covalent or covalent bonding. This mention is just to note the importance of chemistry involved in the already reported synthesis as well as to be considered for the new proposals. Moreover, further constraints related to stability and dispersibility over time should be considered. In this context, noble metallic nanoparticles, stabilized by various stabilizers after synthesis, can be tuned to promote polymeric growth on their surfaces. Gold nanoparticles obtained by reduction reactions using sodium citrate are very stable in aqueous colloidal dispersions [39]. However, within

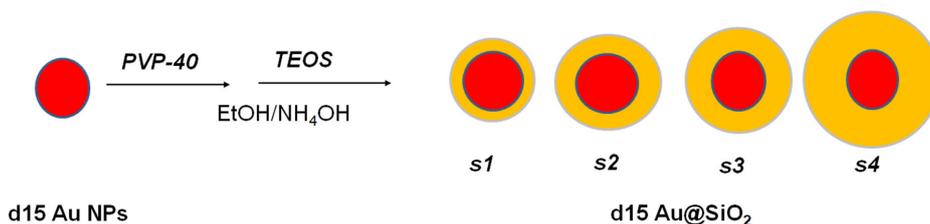
more apolar media related with varied monomeric organic and inorganic structures show variable development of aggregation. This limitation was overcome by adjusting the stabilizers according to the medium used in the subsequent step of polymeric shell addition [40]. For example, the silanization of gold core templates is highlighted, where the first step of the reaction involves applying a PVP coating in an ethanol medium. This modification stabilizes the nanoparticle within an appropriate media for polymerization of different types of modified organosilanes (Figure 3).

In this way, the silica spacer shells can be tuned by controlling the organosilane monomeric species, resulting in well-defined spherical gold Core-shell structures with varying diameters (Figure 4). In this manner, it was afforded to the control of the silica spacer shells. Different samples, designated as s1, s2, s3, and s4, correspond to silica spacer thicknesses of 5.0 nm, 10.0 nm, 16.0 nm, and 25.0 nm, respectively (Figure 3(a)–(d)). These represent typical reactions aimed at spacing the nanoplasmonic surface from the outer layer in contact with the surrounding medium.

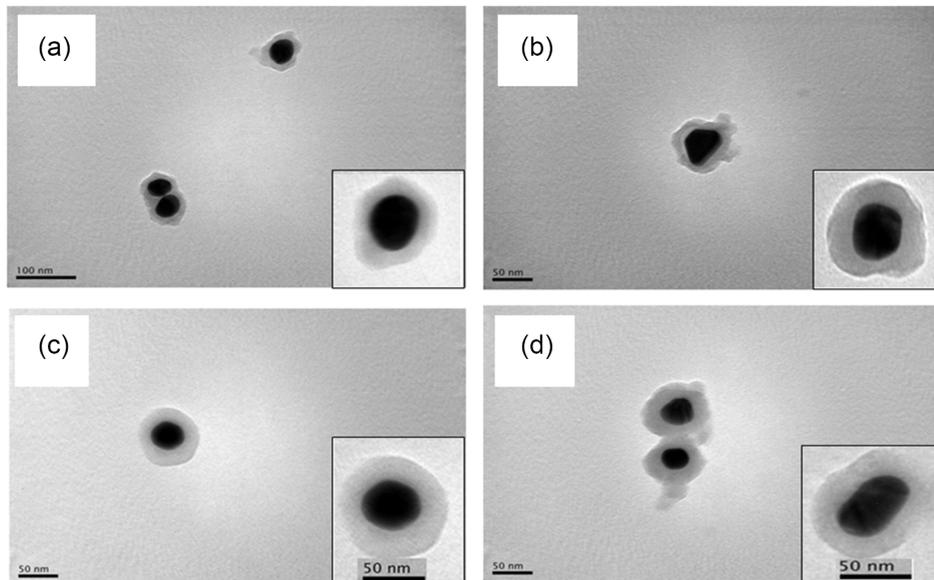
In these nanoarchitectures, it was possible to show a high sensitivity against positioning a second fluorescent layer based on metal enhanced fluorescence (MEF) within few nm intervals of values [41].

As concluding remarks focused on this specific nanoarchitecture, the use of solid inorganic cores offers numerous advantages derived from their intrinsic material properties, including: (i) well-defined sizes and shapes; (ii) relatively easy shape tunability through established synthetic pathways, with manageable challenges when modifying synthesis based on nanochemical surface modifications; (iii) favorable optoelectronic properties; (iv) plasmonic behavior; (v) semiconductive characteristics; (vi) associated quantum phenomena, along with both well-established and emerging physical effects currently under investigation; (vii) a hard and stable material constitution; and (viii) compatibility with a wide range of soft materials, etc. In this context, the interesting material characteristics for opto-electronics and nano-optics in relation with soft and hard matter were noted. In this context, the capability to control the nanoscale of carbon-based nanomaterials such as graphene is highlighted. This compound could provide versatile chemistry nanosurfaces that provide a nano- and quantum-sized template for further layers in addition to optical active materials. Graphene has recently been involved in numerous developments related to Core-shell semiconductor nanoarchitectures, particularly those aimed at achieving efficient photocatalytic performance. These advancements are closely linked to the electronic wave characteristics arising from both 2D and 3D bottom-up fabrication strategies [42]. However, optical properties are developed from graphene and related nano- and quantum materials. In the perspectives of optical structures, there were not so many associated with Core-shell nanostructures. The graphene can be

**Figure 3**  
Steps of templated synthesis of gold cores-shells nanoparticles. The first step was to obtain the citrate stabilized gold cores of 15–20 nm of diameters within aqueous colloids to then PVP coating within ethanol in order to accomplish the tetraethyl orthosilicate (TEOS) modification



**Figure 4**  
**TEM images of Core-shell nanoparticles, Au@SiO<sub>2</sub>, synthesized by the Störber method with different silica spacer lengths (a) 6 nm, (b) 14 nm, (c) 20 nm, (d) 25 nm**



**Note:** The dark colors were related with a gold core with electronic density while the surrounding with optical transparent polymers of modified silica.

formed by single- or multilayered graphene nanosheets, graphene oxide, or reduced graphene oxide. These different chemistries provide alternative ways of covalent and non-covalent linking with other optical active molecules. In addition, below the nanoscale, graphene quantum dots can be tuned to exhibit optoelectronic properties that follow distinct pathways compared to those observed in 2D graphene layers. In addition, the manipulation of these scales could tune pseudo-electromagnetic fields. These electromagnetic fields generated particular variations on different phenomena depending on other parameters such as 3D structures, inter-atom, and surface interactions, as well as to join to other atoms, molecules, and nanomaterials. Thus, a wide range of associated phenomena can be investigated in noble metals and carbon-based nanomaterials, where electronic wave interactions play a central role. In this manner, by controlling electron sources and graphene bi-layers, the ballistic transport of electrons through perpendicular electromagnetic fields was achieved [43]. Electronic waves nominated as mini-bands in long range ballistic transport at low temperatures were measured. This phenomenon was controlled by voltage bias application between the bi-layers that generated tunable electronic valleys. These are just mentions to highlight intrinsic properties of graphene within the nanoscale that could afford towards new opto-electronic manipulations and properties based on Core-shell nanoplatforms in the near future.

### 3.3. Core-shell structures modified with small molecules, short spacers, and molecular chains

The short molecular chains, polymeric branches, and short molecular spacers in general showed to be excellent strategies for varied targeted nanochemistry modifications. The most well-known and intrinsically related within many synthetic pathways of nanoparticles are molecular stabilizing agents modifying nanostructures. The molecules could provide many covalent linking and non-covalent bonding strategies to interact in their

surroundings [44]. It is known that citrate stabilized nanoparticles such as silver and gold are very dispersible in aqueous solutions, could react and go further covalent linking, and exchange stabilizers for other type of molecules and short polymeric chains. As for example, these nanoparticles could be exchanged from citrate to poly-vinyl-pyrrolidones chains in aqueous colloids to then being dispersed within ethanol. This is just an easy manipulation, but it provided many visible and measureable nanoparticle interactions and varied aggregations states. This fact could show how sensitive is the molecular level within the nanoscale (Figure 5).

Other similar examples could be provided from the nanoscale and quantum sizes modifying the known capping agents [45]. Short-chain lipids can stabilize nanoparticles in organic or apolar media, thereby enabling the sensing of various interactions while preserving the intrinsic properties of the inner core for targeted applications or subsequent studies [46].

From this perspective, the potential of modified nanomaterials with diverse molecular grafting is highlighted, enabling dual functionality through the nanochemistry involved, such as: (i) biocompatibility, and (ii) catalytic activity for chemical structure degradation and antibiotic assays via the generation of reactive oxygen species (ROS). For instance, we recently synthesized homogeneous spherical nanoparticles with diameters of 50 nm and 40 nm, tailored for distinct chemical surface modifications and targeted applications (Figure 6).

This simple chemical modification with a small molecule such as citrate permitted to modulate Nanosurfaces within aqueous media and mix with polar organic solvents for targeted functions. In this regard, the design of nano-supramolecular complex synthesis accompanied by switch on/off enhanced fluorescence control and molecular release using a simple chemistry reaction based on the modification of polyethylene glycol (PEG) polymeric chains with di-thiane groups could be highlighted [47]. It was noted that short polymeric chains permitted to stabilize gold nanoparticles linked to macrocycles with the capability to form host-guest complexes with varied molecules upon needs.

Figure 5

Gold nanoparticles synthesis by the Turkevich methods with the addition of sodium citrate in the first step. (i) Then, nucleation of metallic gold arrays form citrate stabilized gold nanoparticles (Au-cit. NPs) in aqueous colloidal dispersion. (ii) Further modification with polyvinylpyrrolidone (PVP) permits to change aggregation state

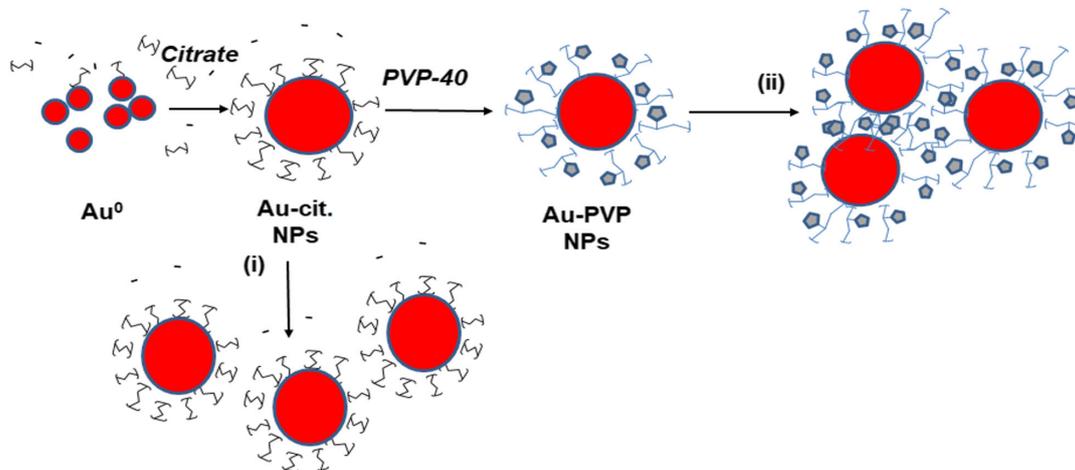
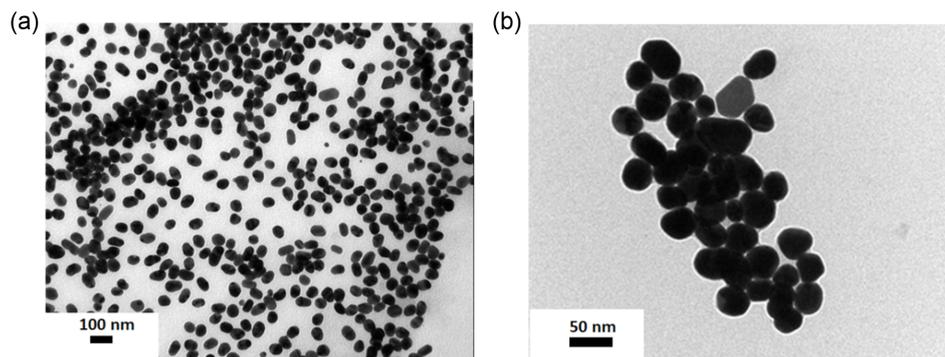


Figure 6

TEM of gold nanoparticles synthesis by the Turkevich method: (a) homogeneous spherical citrate stabilized nanoparticles of 50 nm diameters; (b) zoomed image of gold nanoparticles



In addition, metal-enhanced fluorescence emission and quenching protection effect with host-guest supramolecular structures in the presence of rhodamine B laser dye was showed [48]. In addition, by tuning the spacer chains toward apolar characteristics, modifications were observed in both inter-nanoparticle interactions and their resulting optical properties. In this regard,  $\beta$ -cyclodextrin macrocycles-grafted gold nanoparticles with short molecular spacers showed assembly formation applied for laser dyes sensing. The molecular sensing was based on plasmonic effects and high-intense nano-assemblies were detected by MEF-EP coupling [49]. Thus, these types of Core-shell nanoparticles showed a wide interest with a lot of study and development of prototypes towards Life Science applications such as PEG-grafted metallic, polymeric, and lipid nanoparticles opening to innovation and recent advances in surface decoration of nanoparticles in drug delivery and enhanced nanoparticle absorptions [50].

New synthetic green methods contemplating the use of new reducing agents are highlighted. As for example, the sunlight-mediated green synthesis of silver nanoparticles using Berries of *Ribes rubrum* (Red Currants) could be mentioned. These nanoparticles were evaluated for their antifungal and antibacterial

activities [51]. In a similar manner, many innovative pathways for gold nanoparticle synthesis from natural sources of reducing agents were recently reported [52]. Thus, nano-optics from 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 [53]. Thus, fundamental research focused on single nanoparticles—employing nanophotonics techniques and specialized optical setups—has provided valuable insights and demonstrated practical applications in optically active materials, particularly for use in photovoltaics and solar energy cells. In this context, it was noted that from single nanoparticles were afforded different properties in comparison to collective nanoparticles associations within heterojunctions and luminescent materials [54].

### 3.4. Core decorated with second nanostructured systems

As it was stated in the previous section, the chemical and functional material modification of nano-templates could provide additional variables to take into account in the fundamental and

applied study. Within these new variables, the generation of new nanoarchitectures and epitaxial growth by incorporating further nanostructured materials from different sources could be mentioned. So, in general the Core-shell nanoparticles are nanostructures well-defined related with core templates and multilayered additions that provide homogeneous and smooth nanosurfaces. The different materials involucred govern the optical properties and capability to generate new ones from photon matter interactions. These aspects are no longer novel at this stage; however, introducing the possibility of generating nanostructured shells or spacers opens pathways for the emergence of new modes of electronic vibrations, resonances, and, consequently, light scattering phenomena [55]. From there, even considering the same combination of materials and modifying 3D architectures the nano-optics could be modified. The control of nanoscale features is particularly evident in silicon nanophotonics, where silica-based nanoplatforms serve as a foundation for further functional modifications [56]. Silica nanoplatforms exhibit optical transparency and thereby serve as versatile supports for various functional components, including laser dyes for the development of advanced nano-emitters based on Fluorescence Resonance Energy Transfer (FRET), molecular scattering reporters for Surface Enhanced Raman Scattering (SERS) signaling, semiconductors of diverse compositions, and quantum dots as well [57]. Moreover, it is possible to decorate their nanosurfaces with a nanostructured bottom-up. This architecture could be achieved by adding other types of nanoparticles with different properties. This could be the case of solid spherical and well-shaped transparent silica nanoparticles modified with tiny gold nanoparticles (Figure 7). Further modifications of nanosurfaces at the molecular level could permit to control interactions and assembling affording to new nanopatterned substrates. These nanoarchitectures could be found within colloids as well as to more complex optical active materials (Figure 7(i)).

In this manner, versatile new nanostructured Core-shell architectures with properties not found by other nano-optical approach are generated. It has a cargo space into the silica volume, joined to plasmonics and enhanced plasmonic (EP) properties from tiny sizes. Moreover, there is an augmentation of the available nanosurface per nanostructure with more capability of interactions with other surfaces and soft matter as well. In particular, membranes could be susceptible to incorporate by different mechanisms nanomaterials depending on sizes, shapes of material edges, and surface chemistry. Moreover, these types of nanomaterials are of interest in hard matter for photonics studies and applications. In this regard, the combination of two well-defined and different nanoparticles could provide new bimetallic nanostructured Core-shell type structures (Figure 8). And a new view of potential phenomena is opening by considering topological photonics variables and constrains from inter-nanoparticle interactions [58]. From this combination, multi-plasmonic bands could afford to new opto-electronics capabilities and properties.

By applying this strategy, gold nanoparticles of intermediate sizes can be tuned, with their surface decorated by small gold core nanostructures of a few nanometers. The surface chemistry of these nanoparticles can be modified, transitioning from non-covalent interactions using thiols and their derivatives to covalent bonding through bi-functional linkers, with further chemical modifications also possible. Therefore, it is afforded to a complete modified nano-core template by nanopatterned depositions that generate inter-nanoparticle free spaces with the capability to produce high-intense EP for varied studies and applications (Figure 9).

These nanopatterns could act as hot plasmonic spaces where it is possible to manipulate inter-nanoparticle spaces associated with further plasmonics and quantum phenomena. The distribution of high electromagnetic fields on nanosurfaces could be non-homogeneous resolving varied distribution of plasmonic

Figure 7

**Schema of synthesis of silica nanoplatforms by the Störber method and modified with metallic nanoparticles to form Hybrid SiO<sub>2</sub>-Au NPs. The tiny gold nanostructure on silica provides non-homogeneous plasmonics properties and surfaces for further interactions.**

**Insert figure. (i) It corresponds to hybrid silica nano-arrays**

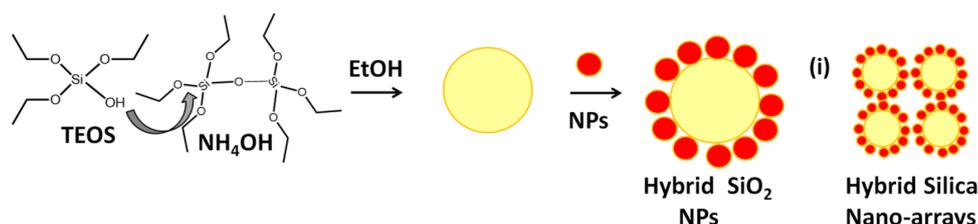


Figure 8

**Schema of synthesis of hybrid metallic NPs. Red and gray colors correspond to gold and silver nanoparticles. It is shown a reduction method for metallic NPs, and representative covalent or non-covalent linking of smaller NPs by incorporation of molecular and polymeric linkers. The nanostructured bimetallic structures combine enhanced plasmonics within different scales and based on different materials**

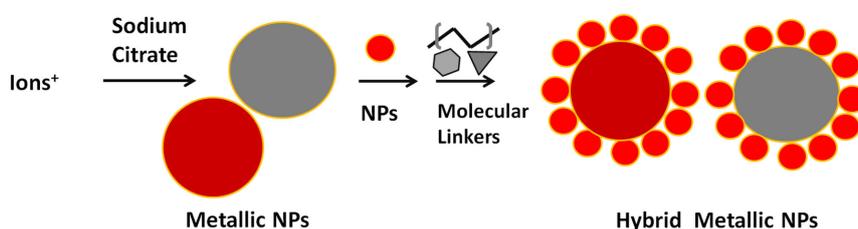
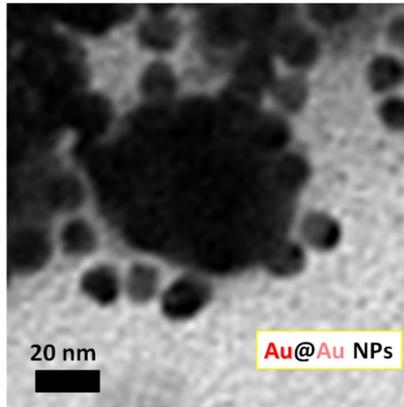


Figure 9

TEM image of hybrid metallic cores modified with a different second nanostructured material. Spherical core-nano-shell particles Au@Au NPs. In this example, it could be observed inter-nanoparticle plasmonic resonances between higher and tiny-sized gold nanoparticles affording to different distributions of high-intense electromagnetic fields



bands generated by the nanopatterned topographies [59]. Thus, enhanced conductions, molecular detections, and nano-emissions with controlled resolutions upon needs could be proposed. These highlights are to note some of the all potential uses of these bi-nanostructured Core-shell nanoparticles.

### 3.5. Cores modified with biomaterials

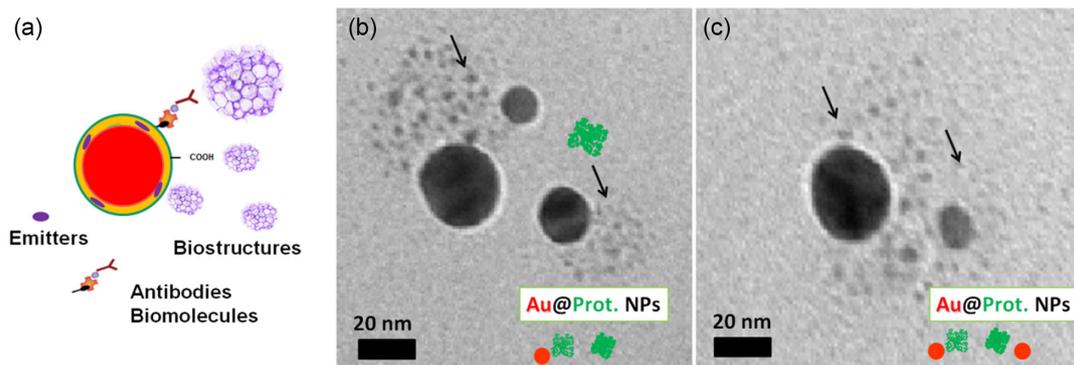
Biomaterials from natural sources and synthetic ones with acceptable biocompatibility are associated with particular properties non-found within synthetic nanomaterials as well as hybrids. The soft characteristics, coupled with heterogeneous interaction points and varying compositions—primarily driven by organic molecules and the occasional presence of inorganic materials—give rise to novel pathways for nanomaterial growth. And, naturally their interest, uses, and applications are different as well. So, Core-shell nanoparticles contemplating the addition of biomaterials could afford to different 3D architectures in comparison to classical well-shaped Core-shell types. The

biostructures could provide asymmetry and specific sites of interactions that produce from spherical and homogeneous distributions to epitaxial growth and topological 3D structures. For these reasons, the design and synthesis considering variable 3D constrains involving different synthetic pathways adjusting conditions such as the use of small molecules and polymers could have targeted interactions with bio-asymmetrical materials. This is just a mention to highlight the importance of prototyping new Core-shell nanomaterials. In addition, it is known that biomaterials synthetic or natural ones show a different behavior within colloids depending on their intrinsic nature and surrounding media. Thus, biomaterials show more frequent asymmetrical structures, with different expositions of functional groups that add more variables in the interaction of the core nanotemplate. However, this variability also leads to diverse targeted applications and phenomena, each of which can be exploited in different contexts. In this regard, biomaterials could be formed by different intrinsic natures adding respective properties and functions. So, this combination of soft/hard materials is a versatile and powerful source of new optical properties with very interesting perspectives to develop applications. For instance, small amino acids, peptides, proteins, and more complex biostructures such as genomic structures could serve as key biomaterials in multilayered approaches [60]. In a similar manner, synthetic biomaterials are considered potential ones to form Core-shell architectures such as from oligonucleotides to origami structures of varied sizes [61]. Moreover, natural and synthetic biocompatible polymers with variable compositions and even considering hybrid biomaterial structures could be noted [62].

So, the Core-shell prototype could be schematized by a solid core formed by different materials and chemical surface modifications. These architectures permitted the conjugation of the biostructures (Figure 10(a)). The versatility of the core template, combined with various linkers and the high variability of the bio-counterpart, adds significant synthetic Nano-Bio diversity, enabling new studies and the development of Nano-Bio-functionalized materials. At the same time and being part of the design, natural and synthetic biomaterials could act basically as homo-functional and bi-functional linkers of nanoparticles (Figure 10(b)). One of the well-known complementary and strong non-covalent interactions that merited a Nobel Prize [63] for an applied Immuno-enzymatic technique known as ELISA (Enzyme linked immune-adsorbent assay) was the biotin-streptavidin

Figure 10

Bio-conjugated layer modification of gold Core-shell NPs applying different biomaterials: (a) schema of gold core tiny silica shell surrounded by varied bioconjugates with different functional biomaterials such as emitters, antibodies, biomolecules, and biostructures, etc. (b) TEM images of tiny gold Core-shell nanoparticles modified with aggregated biotin-streptavidin structures (Au@Prot. NPs). (c) zoomed nano-dimers formation of Au@Prot. NPs



structure [64]. This protein-based structure with a natural folder to host 4 streptavidin per biotin permitted to tune many nano-bio-prototypes and applications based on targeted nano-bioconjugation and assembling of varied particles, highlighting the dimerization and controlled 3D structures with the development of new nano-bio-optics (Figure 10(c)).

In this context, the recent reported bi-colored enhanced luminescence imaging generated by a nanostructured human serum albumin (HSA) conjugated with tiny nanoplasmonics core templates is highlighted. These nanoarchitectures showed particular epitaxial growth forming longitudinal assembled nanostructured HSA gold Core-shell nanoarchitectures. The nano-assemblies showed enhanced luminescence based on MEF coupled with low quantum yields from HAS. Thus, remotely laser excited it was afforded to targeted switch on/off laser coupling for biosensing applications [65]. It should be highlighted that this capability to form asymmetric and longitudinal structures was afforded by non-covalent interactions between silanol groups grafted on tiny gold nanoparticles and external protein sites of the nanostructured HAS. In this way, further experiments are in progress in order to dilucidate sources of asymmetrical interactions and effects on non-classical light modes.

In addition, Core-shell bio-structured materials could be designed by an inverted way considering biomaterials core templates modified with further synthetic and different nanostructured materials creating new prototypes of Core-shell nano-biostructures [66]. The most well-applied use of biomaterials could be bioconjugation techniques using varied biomaterials sources. Therefore, hybrid nanomaterials are obtained with potential Life Science applications. However, it could be used for developments of nanomedicine, nano-pharmacy, biophotonics towards nanophotonics and green photonics where clean energy or biocompatible approaches are needed to develop enhanced nano-photovoltaics [67].

In this manner, the nanoarchitecture could show a versatility not found from other architectures. Thus, the biomaterial adds cargo functions, enzymatic mechanism, new bio-photonic approaches where the source of photons comes from the biomaterial with potential perspectives to enhanced and higher performed opto-electronics. Living lasers and biolasers could be targeted challenges to develop using biomaterials in the near future. In similar manner, the developments of new remotely laser-assisted luminescent particles for tracking targeted further functionalities or phenomena. So, the incorporation of synthetic and natural sources should be considered for multifunctional targeted applications, where enhanced performances are required.

### 3.6. Cores decorated with quantum materials and quantum Core-shell nanoarchitectures

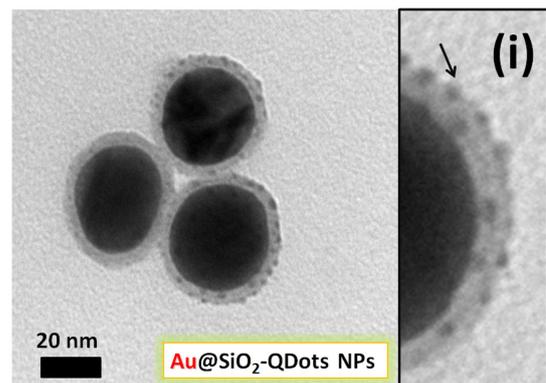
Core-shell structures from the quantum to the nanoscale considering quantum materials from the core to outer shells are well developed. However, the concept was not completely developed to tune further quantum and nano-optics. In fact, quantum dots are well developed using the concept of quantum material cores stabilized with external stabilizing molecular shells known as capping agents [68]. And it is known that the impact of these capping agents could amplify and tune emissions below the nanoscale to beyond. In fact the last Nobel Prize in chemistry was awarded for the design and synthesis of quantum dots [69].

In this regard, the importance and high interest towards innovation within semiconductive nanomaterials where luminescent materials are under focus is highlighted. Thus, the material constitution from luminescence generation by classical emission of individual molecules with optical excitation to inter-molecular fluorescence resonance

energy transfers [70, 71] and other non-classical light states [72], and emissions should be highlighted [73]. Moreover, quantum emitters such as organic [74] and inorganic [75] quantum's dots [76] are of high interest from nano-optic point of view due to their tiny sizes and powerful opto-electronics capabilities confined. In this context, it was reported the enhancement of inorganic quantum dots by metal enhanced fluorescence (MEF) by stabilizing their excited state and improving excitation rates [77]. It is noted that the enhancement of luminescent emitters with higher quantum yields (QY) is not so easy; however, improvements with inorganic quantum dots on silver nanostructured surfaces was achieved [78]. These results showed interesting perspectives towards other types of integrated quantum materials within Core-shell nanoarchitectures. These could be applied to Carbon Dots (CDots) [79], and CQDots [80]. In particular, allotropes of Carbon such as graphene within the quantum scale were highlighted. Graphene QDots showed very stable emission properties accompanied by semiconductive properties as well based on their electronic band gaps [81]. Thus, graphene, derivatives, and further carbon-based allotropes augmented the attention from the synthetic point of view considering the enhancement of quantum opto-electronics [82] and biocompatible materials for high resolved potential imaging uses. In addition, the capability to deliver light affords to the development of biophotonics applications [83]. In this regard, there is an open window of potential further fundamental and applied research considering coupled phenomena as well. Recent studies have highlighted organic materials with confined electronic properties, such as Carbon Quantum Dots, which exhibit potential interactions with the near field of metallic surfaces and nanoparticles. These types of quantum nanomaterials showed high quantum yields [84] with potential applications for bioimaging [85] and bioconjugation applications [86]. Further studies are of interest focusing on biocompatibility [87], low cost procedures in the fabrication, and incorporation in nanomaterials with high social impact such as solar cells [88]. So, the versatility of Core-shell Nanoarchitectures as enhanced platforms is huge; and proofs of concepts are under tuning prototyping different prototypes (Figure 11).

The nature of quantum materials that can be incorporated as nanoscopic templates is of significant interest, owing to the diverse chemistries and strategic approaches available for their

**Figure 11**  
**Gold Core-shell quantum silica shell modified quantum dots (Au@SiO<sub>2</sub>-QDots). Inserted image (i) shows modified silica shells with QDots. The tiny quantum dots provide varied properties related with emissions and opto-electronics placed at accurate distances from the nano-plasmonic core controlled silica spacer shells in this case**



conjugation within the targeted architecture under discussion. Thus, it could be noted that grafted silica nanoparticles with photo luminescent carbon quantum dots synthesized from natural sources [89]. In this manner, the covalent decoration of silica with carbon frameworks has been highlighted, enabling the modulation of the wide band gap of amorphous silica at the nanoscale and resulting in intense and distinctive photoluminescence. From this design, it was suggested that the silica-Carbon quantum dot particles showed inherent advantages of both silica and carbon quantum dots joints for biomedical applications.

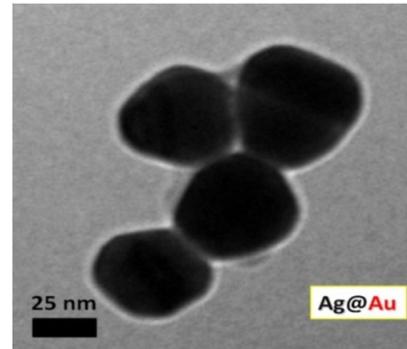
In this regard, it is highlighted that the different decorated quantum Core-shell nanoarchitectures produce different emissions and opto-electronics properties in comparison to other Core-shell types comparing similar sizes as for example. The control over the various optically active components within the architecture, along with the generation of distinct physical phenomena, leads to variations in key optical properties such as resolution, scattering behavior, laser emission effects, and others.

### 3.7. Bimetallic Core-shell nanoparticles

Metallic nanoparticles have shown many optical properties of interest to consider for nano-templates of Core-shell nanoparticles in different research fields. Despite their excellent tunable optical properties, ongoing research continues to focus on the development of novel hybrid nanomaterials and multifunctional nanoplatforms. In this context, it was noted for many authors that bimetallic Core-shell nanocrystals produce new challenges accompanied by opportunities from the different intrinsic matter compositions [90]. However, in the intrinsic ideal design of Core-shell could occur a interactions between both metals in the targeted nanoarchitecture. In this way, the nanosurfaces and cores should be spatially separated at the nanoscale to prevent excessive dissipation from the core before it reaches the surface. But, it is known that the infiltration of such influence is often the interpenetration of matter across both sides due to metal inter-diffusion and/or co-reactions. The key factors to control are in the techniques and methods. Among these, seed-mediated growth can be briefly highlighted as one of the most versatile and well-controlled methods employed. It separates the deposition of the shell from the synthesis of the core (nanocrystal seed) due to the procedures and well-separated and defined steps. However, it is also noteworthy that galvanic replacement reactions may occur between the seed and a precursor, potentially leading to the formation of a bimetallic alloy shell and a more complex surface composition. Nevertheless, as demonstrated here and supported by existing knowledge, such reactions can be effectively controlled. The purpose of not mixing both materials is to maintain their distinct and well-defined properties, allowing their interaction to give rise to new characteristics, such as those observed in alloy formation.

Thus, the incorporation of Core-shell architectures based on bimetallic nanoplatforms are of high interest due to the possibility to stimulate multi-modal energies. In this context, it is known that nanoarchitectures such as bimetallic silver-gold Core-shell nanoparticles are possible to synthesize with relative ease wet chemistry procedures (Figure 12) [91]. In a similar manner, gold – silver nanoarchitectures—as well as other combinations of noble metals and semiconductors—can also be explored. In this way, studies and applications can be developed where different plasmonic resonances are incorporated, enabling the tuning of various plasmonic bands across the entire electromagnetic spectrum. This means that the resonance energy can be tuned according to specific requirements. This is the challenge, and there is at this moment a huge interest to focus on non-classical light in different interval of wavelengths [92].

**Figure 12**  
**Bimetallic silver core-gold shell nanoparticles captured by TEM.**  
**The nano-spheres showed slight differences of electronic densities between silver and gold, however by nanospectroscopy and spectroscopy is possible to record both overlapped plasmonic bands with interferences**



Tuning plasmonics not only enables the control of high-energy fields generated at the nanoscale, but also allows for the manipulation of their spatial distributions. In this perspective, there are many strategies to control spatial bottom-up from the nanoscale to the micro-scale. However, as example of the versatility of Core-shell nanoarchitectures, it was noted recently the innovative design to manipulate reversible shapes and plasmonics tuning of hollowed Ag/Au nanorods [93]. The internal structure of hollow Ag/Au nanorods created by partial galvanic replacement was manipulated reversibly by scanning transmission electron microscope (STEM) probes [93]. Thus, the nanoarchitecture modification with electron energy-loss spectroscopy (EELS) (Figure 13(a)) without disturbing the internal structure was mapped.

Therefore, by the electron beam irradiation the solvated electrons and reactive radicals in an encapsulated solution-filled cavity into

**Figure 13**  
**(a) Write/read cycle and reversibility of interior restructuring in partially hollow AgAu nanorods. Ag migrates toward the beam when a solution-filled volume is illuminated. The void position and its effect on plasmon resonances can be interrogated without restructuring by acquiring electron energy-loss spectra (EELS) from the surroundings of the nanorod. (b) Successive reshaping states of the inner structure show reversibility of the hollowed plasmonic nanorod**

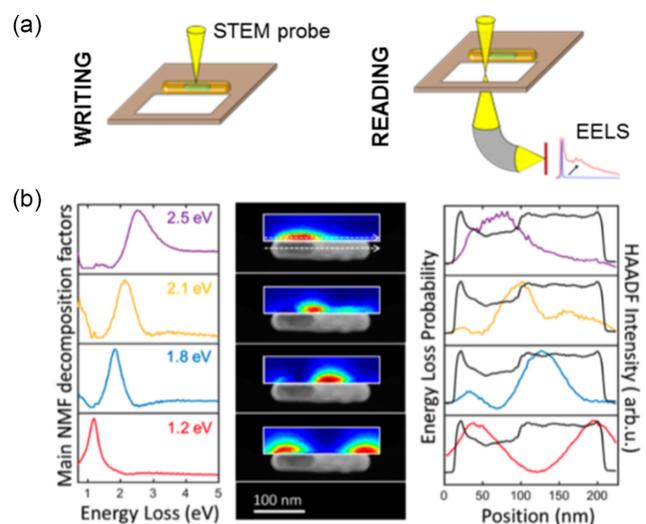
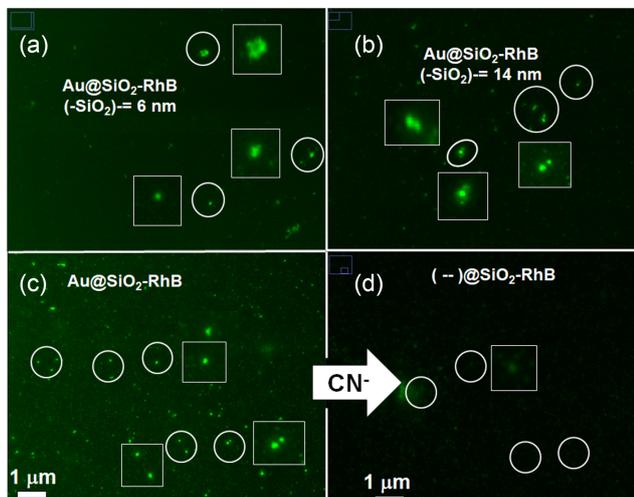


Figure 14

Laser fluorescent microscopy of (a) Au@SiO<sub>2</sub>-RhB, silica spacer 6–7 nm (b) Au@SiO<sub>2</sub>-RhB, silica spacer 14 nm (c) Au@SiO<sub>2</sub>-RhB, silica spacer 14 nm. (d) core-less nanoparticles, (-)@SiO<sub>2</sub>-RhB obtained after sodium cyanide addition. [RhB] = 0.073 μM



nanorods was created. Thus, Ag ions were reduced nearby the electron beam reshaping the core of the nanoparticles without affecting the external shape. Using EELS, the variable real-time energy loss and its positional shifts, along with the reversible reshaping along the nanorod structure, were measured (Figure 13(b)). So, this new hollowed nanomaterial opened potential applications in reprogrammable sensors, responsive materials, and optical memory units. The liquid-filled nanorod cavity offers new opportunities to tune high-intense electromagnetic fields for in situ microscopy techniques and chemical reactions.

In this context, to highlight the sensitivity of phenomena associated with tuning high electromagnetic fields coupled to nearby emitters, enhanced emissions based on Metal-Enhanced Fluorescence (MEF) were demonstrated using Laser Fluorescence Microscopy [94].

From these results could be highlighted different silica spacer lengths incorporated on core templates (Figure 14(a) and (b)) producing variable increases on fluorescence emissions based on MEF [95]. Lower emission intensities were recorded at shorter (5–6 nm) and longer (25–30 nm) distances, as shown in Figure 14(a), compared to the intermediate silica spacer lengths of 10–14 nm, which yielded the highest emission intensities (Figure 14(b)). Moreover, it was highlighted drastic diminutions of intensities after digestion of gold cores obtaining core-less nanoarchitectures (Figure 14(c) and (d)). These results correlate with theoretical studies where the electromagnetic field was calculated and where a maximum local field factor between 2 and 10 nm silica spacers was estimated [96]. These structures highlight several characteristics associated with the solid and smooth surfaces of different combined metals, which can facilitate plasmonic interactions and enable multi-plasmonic responses, potentially yielding multi-colored enhanced emissions tailored to specific requirements. In this regard, current research is under focus and showing varied applications towards bioimaging, bioelectronics, and biophotonics [97].

#### 4. Concluding Remarks

The Core-shell nanostructures and even micro-structures showed a diverse spectrum of possible different spatial distributions of optical components based on a proper combination of controlled matter constitution. Thus, it was shown polymeric structures, metal-polymeric joints, hybrid structures with incorporation of tiny nano-, and quantum

materials, nanopatterned surfaces on Core-shells, bimetallic particles, holed Core-shell architectures, and multilayered nanoarchitectures, etc. Therefore, it is seen a wide view of potential strategies to place the different materials with optical active properties. In this way, functional layers can be developed to interact in close contact, thereby enabling the induction of various energy mode translations. In this point, it should be stated that the mention of varied energy modes is related with different energy levels associated with different wavelengths, frequencies, and physical phenomena. From a physics perspective, various optical phenomena are highlighted, ranging from simple light scattering by spherical particles to more complex resonance modes arising from asymmetric light interactions and non-homogeneous dispersions. Moreover, additional phenomena—referred to as enhanced effects—arising from optical coupling should also be taken into consideration. This could be the case of enhanced light scattering and high impact research and applications as laser Raman scattering. These previous mentions were just considering the scattering of photon and electrons; however, the close interactions and other physical phenomena are involved. In this regard, phenomena such as enhanced luminescence, phosphorescence, chemiluminescence, quantum emissions, laser light generation, and other effects associated with energy transfer between donor and acceptor elements are noted.

So, it is important to highlight the versatility afforded by the incorporation of bimetallic structure placed at accurate distances due to many advantages for targeted applications and variables of interest for fundamental research. It is mentioned as follows considering an augmentation of the complexity of phenomena involved such as (i) versatile tuning of chemical surfaces on nano-core templates, (ii) incorporation of two different opto-electronic properties, (iii) dual plasmonics behaviors, (iv) generation of new multi-modal energy bands from inter-layer interactions, (v) tuning new nano-optics considering remote control by laser stimulations, (vi) development of enhanced phenomena under study such as MEF, FRET, SERS, light scattering, enhanced plasmonics, (vii) nano-anthem effects tuning both plasmonics properties, and considering (viii) semiconductor behaviors and related phenomena as catalyzer surfaces where electron based mechanisms are involved.

In this manner, it was presented these versatile optical platforms from individual nano-optical elements to assembled ones within arrays and further optical set-ups where Core-shell structures provide particular intrinsic light and electron pathways. From individual to collective resonances, various enhanced optoelectronic and non-classical light pathways have been proposed. And, by this way it is expected to develop unique properties that by other strategies are not possible. So, there are a lot of proof of concepts, applications, and patents. However, there is still a huge potential towards fundamental research from where it comes the next generation of applied Nanomaterials.

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## Ethical Statement

This study does not contain any studies with human or animal subjects performed by the author.

## Conflicts of Interest

The author declares that he has no conflicts of interest to this work.

## Data Availability Statement

Data are available from the corresponding author upon reasonable request.

## Author Contribution Statement

**A. Guillermo Bracamonte:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

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