Gold Nanoparticles Chemical Surface Modifications as Versatile Nanoplatform Strategy for Fundamental Research towards Nanotechnology and Further Applications

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Abstract

In this communication it was presented gold Nanoparticles as versatile Nano-surfaces for chemical modifications with targeted functionalities within large spectra of applications. In this perspective, it was showed and discussed about how from well-known synthetic methods by wet chemistry could be developed different types of Nanoarchitectures. Thus, from single molecules depositions towards variable molecular chains could afford to varied interactions between them with consequent different Nanoaggregation states. In this context, it was showed by different instrumental techniques for their characterization. Moreover, polymeric shells could be added in similar manner to create core-shell Nanoparticles. The Core-shell Nanoparticles depending of their chemical surfaces could generate as well different interactions to form controlled Nanoaggregation. In this manner, from colloidal dispersions could be managed depending of interest physical and chemical properties to be translated towards fundamental Research as well as to targeted applications and Nanotechnology. These types of developments and insights within Nanophotonics, Optoelectronics, Bioelectronics, and Biophotonics were discussed.

Keywords: Gold Nanoparticles; Nanosurfaces; Wet chemistry; Chemical surface modifications; Core-shell Nanoparticles; Nanotechnology; Nanophotonics; Biophotonics.
Introduction

There are many Nanomaterials actually in current development depending on chemical and physical properties studied from fundamental research point of view as well as applied research and targeted Nanotechnology developments. However, there are not so many with particular properties as it is observed from gold Nanostructures [1].

It is a relative stable Nanomaterial in many conditions, Biocompatible in controlled conditions too, and it is interesting its electronic properties for chemical and physical studies and applications [2]. These properties permit to tune their Nanosurfaces by many different ways based on the electronic configuration that permit easier polarization in presence of electrophoretic chemical agents that could interact with variable electronic densities. By this manner, it was afforded to many strong non-covalent linking on Nanosurfaces by varied small organic molecules, inorganic chemical agents, and variable chemical chains, polymers, and biomolecules too [3,4].

Moreover, these properties permitted the deposition of monomeric forms and polymeric growth to cover Nanosurfaces and generate variable polymeric spacer shells [5]. These Core-shell Nanoarchitectures showed different new properties and applications [6]. Therefore, it was made a multifunctional hierarchical structural from the gold Core as template and support with the incorporation of additional functional and layers accompanied with high sensitivity [7]. By this manner, it was studied, evaluated and discussed in many research works focused on varied Nanoplatforms for constructing new approaches to cancer treatment, imaging, and drug delivery [8].

All the Nanoarchitectures involucrated, such as modified gold Cores templates with molecular spacer with variable dimensions, and Core-shell Nanoarchitectures, based on their chemical surfaces, sizes and shapes, could afford to variable and controlled interactions between them depending of their chemical modifications. From these interactions, different states of Nano-aggregations could lead to different new physical phenomena non-studied yet, as well as many already studied with potential applications within Nanotechnology and Life Sciences. As for example, it could be mentioned the decoration of gold Nanoparticles with ovalbumin-derived epitopes with consequent immune responses on T-cells by varying sizes and shapes [9]. Therefore, in this brief communication, it was intended to report about these new properties from controlled hierarchical gold based Nanoarchitectures for further discussion towards new developments for Nanotechnology focused on Nanophotonics, Optoelectronics, Biophotonics, Nanomedicine and other themes and topics related (Scheme 1).

Synthesis of gold nanoparticles

Different synthetic methods could be found in literature by wet chemical methods; however most of them are based on reduction reaction of gold ion sources. In this context it could highlighted the Turkevich method [10] by the use of citrate as reducing agent of Au$^{3+}$ (Scheme 2). This methodology was largely applied as well as revised in order to optimize and control the synthesis [11]. By this manner, it is possible to tune variable spherical sizes, and by modified synthetic pathways as well their shapes [12]. However, even if there are many studies related, there are many other non-developed yet, as well as further studies within Nano-Optics, and Quantum Optics in current Nanotechnology Research [13].

![Scheme 1: Representation of gold Nanoplatforms chemical modifications and targeted studies and applications focused on; (i) Nanophotonics; (ii) Nanelectronics; and (iii) Nanomedicine. Reprinted with permissions of A. G. Bracamonte et al. 2022.](image1)

![Scheme 2: Gold Nanoparticles synthesis by the Turkevich method with the addition of Sodium Citrate in the first step. Then nucleation of metallic gold arrays form citrate stabilized gold Nanoparticles (Au-cit. NPs) in aqueous colloidal dispersion (i). Further modification with Poly-vinilpyrrolidone (PVP) permits to change aggregation state (ii). Reprinted with permissions of A. G. Bracamonte et al. 2022.](image2)

![Figure 1: Gold Nanoparticles synthesis by the Turkevich method. (a) Homogeneous spherical Nanoparticles of 50 nm; (b) Zoomed image of Nanoparticles. Reprinted with permissions of A. G. Bracamonte et al. 2022.](image3)
Moreover, there are new synthetic green methods contemplating the use of new reducing agents. As for example, it could be mentioned the Sunlight-Mediated Green Synthesis of Silver Nanoparticles Using the Berries of Ribes rubrum (Red Currants). These Nanoparticles were evaluated their Antifungal and Antibacterial Activities [17]. In similar manner many innovative pathways for gold Nanoparticles synthesis from natural sources of reducing agents were recently reported [18]. As well these type of Nanoparticles are spherical, well-shaped forms, within homogeneous colloidal dispersions. These properties could depend of the reducing agent sources, and purifications of extracts used. In these perspectives, it could be noted spherical Nanoparticles by the addition of acid Guanidinium Thiocyanate–Phenol–Chloroform (GTPC) fraction (= bRNA) in Au(III) chloride (HAuCl4) solution [19]. Thus, it was recorded Electron-dense particles scattered nearly spherical in the interval of 10-20 nm of diameters (Figure 2).

In order to conclude this subsection, it should be highlighted the experimental fact observed related with the easy formation of gold Nanoparticles in aqueous media, as well as organic media by modified methods [20] using organized systems to stabilize gold nucleation arrays [21]. In both cases well shaped spherical Nanoparticles were obtained; however different chemical surface modifications could be applied. And by this manner, depending of requirements for the next Nanotechnology development, it could be used one or the other strategy.

**Chemical surface modifications of gold nanoparticles**

The chemical surface modification of metallic gold basically is based on the polarizable electronic surfaces and favoured interactions of some targeted elements, molecules, and molecular monomers for polymerization reactions developments. For gold Nanosurfaces, these strategies are applied contemplating as well inter-Nanoparticle interactions by Wander-walls interactions, and stabilizing agents interactions too; depending of the reducing agent and media used [22].

Thus, it should be highlighted the use of sulphur based functional groups, and molecules. This particular atom incorporated in different molecules has being already shown a lot of Nanosurface modifications [23]. This is a non-covalent interaction that could be considered as strong covalent bond [24]. It is applicable in aqueous media and within aqueous/organic media too. As for example, by this manner it was afforded to modified gold surfaces with alkane thiols, and modified organic molecules containing thiols [25]. By this manner it was obtained varied modifications of Gold Nanoparticles for Biology and Medicine; such as from citrate, CTAB, amines to transferrine, oligonucleotides, peptides, antibodies, and lipids for different applications as for example cell uptake, gene transfection, antiviral activity, nuclear translocation, imaging, cholesterol, and Photothermal therapies [26,27].

In addition, small polarizable molecules containing heteroatoms such as pyrrolidone, pyridone, pyperidine, pyridine derivatives are potential chemical linkers for gold Nanoparticle modifications [28]. Therefore, it could be tuned Nanosurfaces with different chemical species joined to other organic functional groups for further chemical modifications. The first added molecular layer could be the targeted structure for the study of interest or application; however in many cases it is the molecular linker and stabilizer agent for the next hierarchical architecture within the desired Nanostucture [29].

Moreover, metallic gold surfaces are very stable and proactive interacting sites with other heteroatoms that maybe are not so strong to form stable non-covalent linking [30], but as stable to interact and react with other molecules [31]. Therefore, it could be leaded to fast polymeric chains reactions to form multilayered modified surfaces [32]. From this concept and design it could be proposed varied new approaches for further studies and applications incorporating different material properties (Figure 3). The multilayer deposition could afford within colloidal dispersion to Core-shell Nanoarchitectures [33] that it is discussed in the next section.

**Figure 2:** Green gold Nanoparticles synthesis by the addition of acid Guanidinium Thiocyanate–Phenol–Chloroform (GTPC) fraction (= bRNA) in Au(III) chloride (HAuCl4) solution. (a) TEM images of freeze-dried precipitates obtained from mixture of bRNA and HAuCl4 solution; (b) Zoomed image of Nanoparticles. Reprinted with permissions of T. Kunoh-J. Takada et al. ACS Sustainable Chem. Eng2018.

**Figure 3:** Gold Nanoparticles synthesis by the Turkevich methods with the addition of Sodium Citrate and stabilized with PVP in a second step as short molecular spacer.Reprinted with permissions of A. G. Bracamonte et al. 2022.
Gold core-shell nanoparticles

Gold Core-shell Nanoparticles are formed by a core template surrounded by a continuous polymeric shell [34] that afford to a tuneable well-ordered multi-material design with an accurate size and shape of each part of the structure [35]. This Nanoarchitecture could be designed from varied shapes based on tuneable gold Cores applying different synthetics methods as it was mentioned previously. For example, spherical gold Core-shell Nanoparticles permits to design variable dimensions with varied available Nanosurfaces to interact and react with the close surrounding media (Scheme 3.i). By this manner, Multi-layered Nanoarchitectures [36] could be obtained with different functionalities applied for fundamental Research and Applied studies as well (Scheme 3.ii).

(i) Au@SiO$_2$ (ii) Au@SiO$_2$-LDye (iii) Au@SiO$_2$-LDye@

Scheme 3: Scheme of gold Core-shell Nanoparticles: (i) Mono-layered gold Core-shell Silica Nanoarchitecture (Au@SiO$_2$); (ii) Fluorescent gold Core-shell Silica Nanoparticle by covalent linking of a Laser Dye (Au@SiO$_2$-LDye); (iii) Multilayered and Fluorescent gold Core-shell Nanoparticle (Au@SiO$_2$-LDye@). Note: In the design it is represented the addition of two different polymeric shells. Reprinted with permissions of A. G. Bracamonte et al. 2022.

In this manner, it was reported recently by us gold Core-shell Silica Nanoparticles. These Nanoarchitectures permitted the accurate control of silica spacer lengths leading to the addition of variable additional fluorescent shells to exploit the Metal Enhanced Fluorescence (MEF) [37] (Figure 4). In brief, MEF phenomena are based on the Fluorophore Plasmon interaction that produces a higher electronic excited state accompanied with increased emission decay and Fluorescence Lifetime Decays shortening [38-40]. This higher excitation is provided from a higher intense electromagnetic field within the near field of the metallic surface. So, this effect depends mainly of the fluorophore-metal spacer length and the spectroscopical properties of the metal from their intrinsic properties; due to that it is required a fluorophore Plasmonic overlapping and coupling [41].

In order to add this mentioned external fluorescent shell, it could be used modified organosilane with different organic functional groups for covalent linking of Laser organic dyes such as Rhodamine [42]. In this manner it could be achieved well shaped spherical Core-shell Nanoparticles recorded by Transmission Electron Microscopy (TEM) with different silica spacer shells lengths as well as Fluorescent shell lengths with different loaded Laser dyes concentrations (Figure 4).

Applications and perspectives in nanotechnology

As it was exposed previously, within colloidal dispersion it could be achieved varied chemical surface modifications that could affords to different properties depending of tuned materials incorporated. About that, it is mentioned: i) Plasmonic properties associated with high electromagnetic fields, ii) Semiconductor properties, ii) quantum properties, iv) generation of Reactive Oxygen species (ROS), v) Photo-thermal and vi) Opto-Electronics properties. And, moreover other properties and phenomena related, such as Biocompatibility, and Enhanced Plasmonics (EP), as well other ones from combinations and interactions between different physical and chemical properties. In this brief summary of the main properties of the cores it could be already got an idea of potential interests within many studies and applications focused on Nanotechnology.

In addition, the contemplation of an additional shell of varied materials surrounding the core template could contribute with other properties. Thus, as it was mentioned previously, silica shells with excellent dielectric properties and Optical transparent characteristics contribute with intrinsic characteristics that couple previous properties mentioned. In these perspectives Enhanced and improved properties could be developed such as Ultra luminescence generation, brighter Plasmonics Light Emitter Devices (P-LEDS), Resonant Plasmonics structures for Opto-electronic devices within different optical set ups and approaches such as within Microfluidics and Nanofluidics systems and further developments. In this context, the potential development of Nanoptics is in the cutting edge of the knowledge from fundamental point of view focused on Research; but as well due to the capability to generate high electromagnetic fields with consequent interactions through longer distances by new resonant modes and by this manner far field applications. These properties could show high sensitivity that could produce the next generation of smart responsive Nanoplatforms such as for example for Single Molecule Detection (SMD) [43]. These types of Nanostructures showed important effects and applications as well within Surface Enhanced Raman Spectroscopy for Laser dyes with close concentrations values related with SMD [44].
In addition it should be mentioned Optoelectronics properties based on the combination of gold Nanoparticles with other semiconductors as well as the formation of alloys [45,46]. For example it could be mentioned, the design and fabrication of Plasmon Enhanced perovskite metallic photodetectors [47]. The Enhanced properties accompanied with improved performances were achieved by combining gold tringles Nanoantennas with CH3NH2PbI3 film. By this manner, the surface morphology showed an influence in the optical effect of the substrate as it was theoretically calculated as well. Thus, it was recorded a significant redshift in the absorption spectrum accompanied with an increased intensity and luminescence lifetime decay shortening. This result showed potential uses to enhance the intensity of Light Emitting Diodes (LEDs); as well as prolong lifetime of charge carriers in coupled perovskites-metallic Nanoparticle structures for photovoltaics applications such Solar Cells [48].

Therefore, there is an open window of Optical properties that could be developed for a broad number of studies and applications that of high impact and interest within Nanotechnology applications based on gold Nanoparticles and modified structures.

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