__Original Research Article__

Gold Nitrate Nanoparticles: A Candidate for Nanobiotechnology Applications

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ABSTRACT

The research shows that due to the transition from classical mechanics to quantum theory, there have been significant advancements in physics, especially in the ability to manipulate small structures. This gave rise to the fields of nanoscience and nanotechnology, stemming from physicist Richard Feynman's ideas presented in a 1959 lecture to the American Physical Society. In today's world, scientists aim to study these structures because, due to their dimensions, they can be used in various functions, including in the biomedical field. Since then, the search for materials with structures and properties that benefit humans in conducting tests and/or combating diseases has become crucial. In this study, we will present the structural, electronic, and optical properties of gold nitrate nanoparticles through computational modeling using the CASTEP module of the Materials Studio software, employing density functional theory (DFT) as the basis for calculations.

Keywords: Nanoscience. Gold. Biomedicine. DFT.

1. INTRODUCTION

In recent years, a small word with great potential has quickly fallen into the world's consciousness. That word is "nano." This has led to speculation about the changes that would occur in all aspects of science and engineering. It is possible to envision around us that we use increasingly effective products, equipment, and substances with utilities never before imagined. These innovations are partly the result of advances in nanoscience, which is simply the study of the fundamental principles of molecules and structures that are at least one to a hundred nanometers in size [1].

Furthermore, revolutions in these materials have stemmed from the pioneering work of nanotechnology, mentioned by Richard Feynman in 1959 when discussing the possibility of manipulation and control at extremely small scales, inaugurating and anticipating this technological revolution. He concluded that if we could control the arrangement of objects on a small scale, it would be possible to create a variety of properties that matter can have [2]. However, due to the lack of technological resources at the time, the study could not progress. Today, thanks to computational power, we know that nanotechnology allows the control of matter at atomic and molecular levels, dedicating itself to the development of materials and components for various research areas such as medicine, electronics, science, etc. One of its basic principles is to construct new structures and materials from atoms with the aim of creating more stable and better structures than in their "normal" form, occurring because these elements behave differently on the nanoscale.

Moreover, in nanoscience and nanotechnology (N&N), nanoparticles are necessary. These are particles on the nanometer scale and are defined as small objects that behave as a whole in terms of transport and properties. Particles are classified by diameter and may or may not exhibit size-dependent properties that are sometimes very different from those observed in fine particles or bulk materials. Nanoparticles can be obtained through various physical, chemical, and even biological processes, and can currently be synthesized in various forms, such as spheres, cubes, tubes, prisms, octahedra, and more. Each shape has different physical properties (electrical, magnetic, catalytic, melting point, and optical) that can be adjusted by modifying, for example, the ratio between the length and diameter of the nanoparticle [3]. Thus, when used in the production of new products, nanoparticles provide greater efficiency in industries or medical areas.

1.1 Nanoparticles in medicine

Medicine is an area that is constantly evolving, driven by technological advances. Over the years, we have witnessed the development of various technologies that have revolutionized how we diagnose and treat diseases. Part of this progress comes from nanoparticles that, made from different materials, can be designed to carry drugs, contrast molecules, allowing a more precise and efficient approach to the treatment of various medical conditions.

One of the most promising applications of nanoparticles in medicine is targeted drug delivery. These particles can be designed to bind to specific targets, such as tumors, and release the drug in a controlled manner at the desired location. This reduces the toxicity of the drug to healthy tissues and minimizes unwanted side effects [4].

Furthermore, the possibility of using therapies has been studied, one of which is phototherapy, a direct combination with chemotherapy, in which photosensitizers are activated from a radiation source, becoming a safer and more specific application, as nanoparticles will be activated in the body region where a certain wavelength is concentrated.

In addition to this, in photothermal therapy, nanoparticles are activated by a heat source, usually infrared waves, where short or long lengths are applied. After activation by heat, the nanoparticles absorbed in the cells are thermally decomposed, leading to the necrosis of defective cells.

Moreover, with these uses, there has been an increase in research using gold nanoparticles because they have characteristics with great potential for these biomedical uses due to their varied properties with their size.

1.2 Gold nanoparticle

The chemical element gold (Au), with an atomic number of 79, belonging to the transition metals, is one of the most coveted metals widely used in jewelry making. It has numerous applications due to its properties, extending beyond its brightness and color. Gold has a melting point of (1064 °C) and a boiling point of (2856 °C). It exhibits high inert behavior when attacked by corrosion. This property of metals allows for broad applications, and when produced using specialized techniques to obtain nanoparticles, they demonstrate effective catalytic capabilities [5].

Gold is a precious and dense metal that can be found naturally in a pure state. It possesses high inertia, preventing oxidation under the influence of strong oxidants such as nitric acid [6]. Thanks to these properties, gold was one of the first materials to be processed according to its structure. This metal has a golden color, a shiny appearance, corrosion resistance, malleability, and hardness [7]. Gold nanoparticles are identified as solid colloidal particles with an approximate size of 1 to 100 nm, potentially composed of carbon, phospholipids, polymers, and metals [8].

In its solid state, gold appears yellow, but at the nanoscale, gold can exhibit various colors depending on the dimensions of the nanoparticles. For example, particles with 100 nanometers appear pinkish-purple, while those at the 20 nm scale are reddish, and a brownish-yellow color is perceived when the nanoparticles are 1 nm. These color differences arise due to the emergence of quantum effects related to size [9].

Gold nanoparticles are included in the group of metallic nanoparticles, and their application has become possible recently due to new optical equipment, electronic devices, and probes capable of manufacturing and detecting and identifying biomolecules of medical interest. An ancient example of their use is found in the ancient Egyptians who used gold nanoparticles as a suspension, an elixir of longevity, a drink with the property of prolonging youth, and stimulating the mind [9].

Currently, gold nanoparticles have received considerable attention in the field of biomedical applications due to their high biocompatibility and ease of synthesis. Additionally, their ability to modify surfaces and adjust optical and physical properties holds promising potential for future use in photothermal therapies with specific wavelengths, enhancing the destruction of malignant cells [10]. Based on this information and the derivation of gold with the union of nitrate anion, the next section provides important insights for understanding the study material, gold nitrate.

1.3 Gold nitrate

A chemical compound formed naturally when nitrogen combines with oxygen or ozone. It is a chemical compound that contains gold in its molecular structure. It is an inorganic salt composed of gold ions (Au^{3+}) and nitrate ions (NO^{-3}). Gold nitrate can be found in a solid form, usually as a powder or crystals. Gold nitrate, also known as "gold nitrate," has its molecular formula given as $AuH_7N_4O_{15}$, with an average molecular weight of 500.04, and has various properties that make it interesting and useful in various applications. One of its most notable properties is its color, which is typically yellow or orange, depending on the crystallization form. Gold nitrate is also soluble in water and can be easily dissolved to form an aqueous solution of gold nitrate. It is widely used in the process of galvanizing materials, serving as the "gold salt" in electroplating. With this information, a comprehensive study of the properties of its crystal structure can be conducted.

2. METHODOLOGY

To obtain results and answers on the topic addressed in this work, an enhanced methodology was adopted, combining explanatory research methods, exhaustive literature review, and advanced analytical techniques.

To initiate the process, an exhaustive literature review took place, seeking up-to-date and relevant information on the subject. This literature review covered scientific journals, books, and other reliable resources to theoretically support the study and understand the current state of knowledge in the area.

Moving on to gather specific information about gold nitrate crystal, the Biovia module, particularly the CASTEP module, was employed. Its function is to explore the properties of crystals and materials. It was configured for the GGA-PBE pseudopotential (Generalized Gradient Approximation functional, proposed by Perdew-Burke-Ernzerkof), conserved norm, cutoff energy of 750 eV, and 3x3x3 k-points. This configuration allows for calculations of the material's physical properties, enabling us to obtain precise and reliable data on the material under study, such as its structural, electronic, and optical properties.

In the next stage, a quantitative analysis of the results was performed using software for graph plotting (ORIGIN), and with statistical methods, the collected information was interpreted and quantified. This process enables the identification of trends and relationships between the variables studied, providing a solid foundation for analysis.

Parallel to the quantitative analysis, qualitative research was conducted to gather additional information about the material under study and make comparisons. Using information from the studied bibliographies as a reference, qualitative insights were determined regarding the characteristics, properties, and behaviors of the material. Based on these results, an interpretation of the material's applications was made.

Additional information regarding the methodology can be found in the reference [11].

3. RESULTS AND DISCUSSION

The results obtained pertain to the structural, electronic, and optical properties of the chosen material. After optimizations, it was possible to accurately present the available properties of the material.

3.1 Structural properties

The properties of crystals are shaped by the highly ordered geometric arrangement of atoms or molecules in the crystal lattice, allowing the characterization of their structure. For an analysis of the material's properties in its primitive form, it is essential to achieve optimal stability among the atoms composing the unit cell. This process aims to minimize energy, requiring the application of predefined parameters in its geometric optimization. These details are further elaborated in the following sections.

The crystal structure of gold nitrate consists of 108 atoms in its main unit cell, as can be seen in Figure 1, panel (a). In addition to having a primary structure with monoclinic symmetry, point group 2/m, and space group C2/c, respectively, it is important to note that the density of gold nitrate is found to be 2.734 g/cm³. To optimize calculation performance, symmetry parameters were adapted. The lattice parameters after optimization can be observed in Table 1, including their axes and angles (a, b, c, α, β, and γ). Figure 1, panel (b), illustrates the primitive cell in reciprocal space, also known as the Brillouin zone, which was used for band structure calculations.

These details provide insights into the structure of gold nitrate, emphasizing the importance of symmetry parameters and structural characteristics for understanding its physical properties. Furthermore, the analysis of the Brillouin zone allows for the investigation of the material's electronic properties and conductivity, providing valuable theoretical foundations for material analysis.

Table 1.Lattice parameters (a, b, c, α, β, and γ) and volumes (V) for the primitive cell.

	a (Å)	**b** (Å)	**c** (Å)	$\boldsymbol{\alpha}$ (°)	$\boldsymbol{\beta}$ (°)	$\boldsymbol{\gamma}$ (°)	**V** (Å^3)
EXP.	7.63	7.63	12.44	67.95	67,95	70.69	607.31
GGA-PBE	7.632 (-0.1%)	7.632 (- 0.1%)	12.44 (0.0%)	71.27 (4.9%)	71.27 (4.9%)	70.68 (-0.1%)	607.3 (-0.1%)

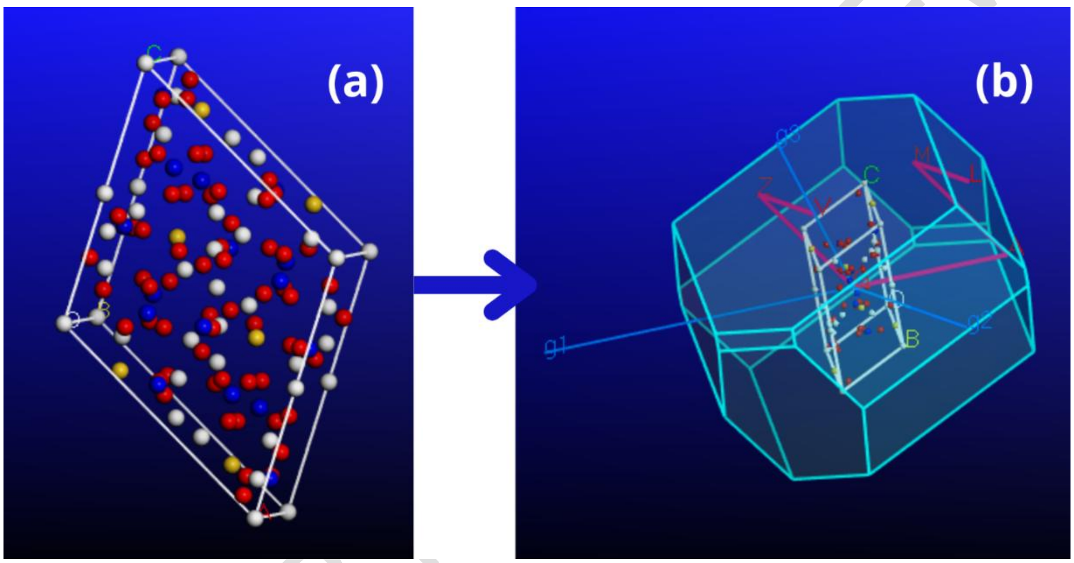

Fig. 1.(a) Crystal structure of gold nitrate (AuH7N4O15), (b) primitive structure of gold nitrate with the representation of the Brillouin zone, including its high-symmetry points and primitive vectors.

3.2Geometry optimization

The geometry optimization of gold nitrate was carried out using the Density Functional Theory (DFT) formalism, employing a Generalized Gradient Approximation (GGA) functional proposed by Perdew-Burke-Ernzerkof, identified as GGA-PBE. Additionally, a norm-conserving pseudopotential was used to ensure the conservation of electronic density during calculations, crucial for obtaining reliable results. Furthermore, a plane-wave basis set with a cutoff energy of 750 eV and a 3x3x3 grid sampling of the Brillouin zone were employed to calculate integrals, determining the resolution and precision of the calculations sufficiently to achieve convergence in the crystal structure. This process considered a tolerance of 0.843 x 10^{-6} eV, resulting in 20 iterations for convergence.

3.3 Electronic properties

In solid-state physics, it is important to understand some concepts that are part of the crystal structure, as properties can be derived from it. Electronic structure is one of these concepts because it allows us to classify materials as insulators, semiconductors, and conductors.

The partial density of states of the material with its orbitals (s, p, d) in the range from -25 eV to 20 eV, as observed in Figure 2. Initially, the s orbital, which lacks orbital magnetic moment, meaning it does not directly contribute to magnetic properties related to the orbital motion of electrons, exhibits its highest peaks in the region around -19 eV. Additionally, the p orbital significantly contributes to the valence bands with two considerable peaks in the regions of -7.55 eV and -1.63 eV. The d orbital, in which electrons have spin and orbital magnetic moment, contributes to magnetic properties related to the orbital motion of electrons, with two minimum peaks in the regions of -4.54 eV and -3.3 eV.

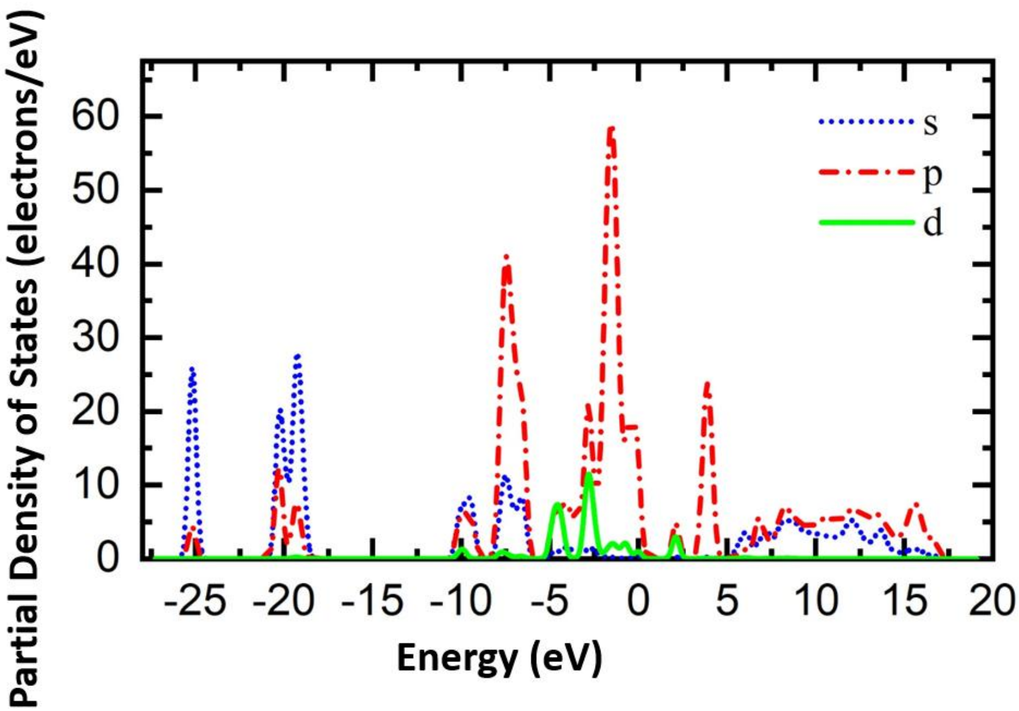

Fig. 2. Partial Density of States (PDOS) of the gold nitrate crystal.

3.4 Optical properties

Optical properties refer to the material's response to interaction with electromagnetic radiation, especially within certain spectra. The optical behavior of solid materials results from their interaction with electromagnetic radiation and wavelengths in the visible region of the spectrum.

When electromagnetic waves reach the surface of an object, one or more phenomena corresponding to its structure can occur. Part of the radiation is transmitted through the medium, another part is absorbed, and the remaining part is reflected at the interface. The success of this material in absorbing is related to the need for photon absorption to promote an electron from the valence band to the conduction band, overcoming the gap and generating the transfer of electrons from the valence band to the conduction band. Thus, by studying the optical properties of the gold nitrate crystal structure, electromagnetic absorption in terms of wavelengths (nm) was observed in Figure 3.

In Figure 3, using the GGA approximation along different crystallographic planes ([100], [110], and [111]) and for a polycrystalline sample (POLY), absorption behaviors in the ultraviolet and visible light are seen. The highest peak in the graph is around 60 nm to 70 nm with an average absorption of 2.37 x 10^5 cm^{-1}, which is in the extreme ultraviolet (EUV). The average peaks are in the region of (UVC) 200 nm to 260 nm with an average absorption rate of 1.0 x 10^5 cm^{-1}, but then they decrease. It also absorbs in the infrared region (700 nm), making it a promising material for photothermal therapy. Photothermal therapy utilizes nanoparticles to generate localized heat when irradiated with near-infrared (NIR) light, as it has the ability to penetrate deeply into the body due to its minimized interaction with water molecules [10]. This therapy aims to destroy diseased cells or tissues. This technique harnesses the unique properties of nanomaterials to efficiently and precisely convert light energy into heat, directing it to specific areas of the body.

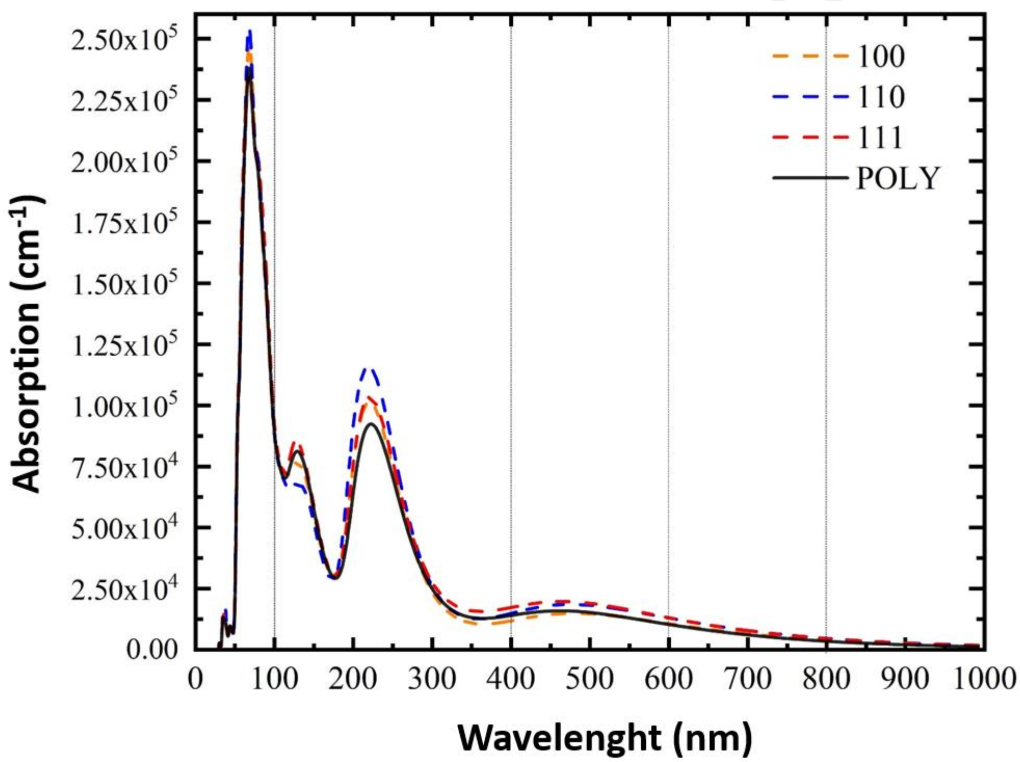

Fig. 3. Optical absorption in various crystallographic directions as a function of wavelength for the gold nitrate crystal in the GGA-PBE approximation.

4. CONCLUSION

We must consider that nanoscience has propelled technology since its inception with Richard Feynman. Thus, there has been a significant advancement in the study of nanomaterials since then. However, due to their size being smaller than a hair strand, the use of quantum formalism for their development is extremely crucial, which implies a challenge as quantum calculations are complex and probabilistic.

In this regard, we were able to gather a wealth of information regarding gold nanoparticles and subsequently conduct simulations for nanobiotechnological applications. Besides, the realization that the use of gold in nanostructured systems indicates a change in its fundamental properties for nanoparticles, making it promising for various purposes.

Thus, through the study of the material, it is possible to discuss the band structure, an essential aspect to explore, as it allows us to determine the regime in which it operates. The material exhibits characteristics of an insulating material, and its partial density of states, based on the values found, indicates a structure without significant magnetic ordering.

Subsequently, we delved into exploring the optical properties of this material, highlighting its notable absorption in the ultraviolet range and a portion of absorption in the infrared spectrum. This absorption capacity opens doors to exciting future prospects, especially in the field of photothermal biomedicine.

Therefore, this material reveals promising potential in the biomedical application known as photothermal therapy. By harnessing nanoparticles, it is possible to convert light energy into localized heat, a technique that promises to revolutionize treatment precision and reduce invasiveness. By precisely directing the generated heat, damage to surrounding healthy tissues is minimized, marking a significant advancement compared to traditional approaches.
In this context, an innovative vision of biomedicine emerges, with the potential to redefine the treatment of a variety of medical conditions. This approach not only promises more effective results but also introduces an optimistic outlook for the future of medicine.

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