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Introductory Chapter: Basic Concept of Gold Nanoparticles

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1. Introduction

Nanoscience and nanotechnology are generally used in the design, production, characterization, and potential applications of nanostructural materials especially considering their size as well as shape. Nanoscience is a phenomenon that occurs in structures of nanodimensions. Generally, the unique features of nanosystems arise exclusively from the small size of the systems. Here, nano is the smallest dimension as it is obtained in the world in various branches of chemistry, physics, drug design, semiconductor materials science, and even biological science. The hydrogen atom diameter is about 1/10 of a nanometer; therefore, the nanometer dimension or scale is the very tiny scale on what we might consider the building objects or machines on the fundamental basis of the principles in where from everyday mechanics. By using the 1000 as well as hydrogen atoms it could be picked into a cubic object. Nanoscience and nanotechnology are cumulative designations referring to each practical technology and instrumental science, which function with nanodimensional scale or objects. Basically, low-dimensional nanoparticles have various significant properties compared to those of larger objects/particles, and these characteristic properties could be utilized in a broad spectrum of areas of medicine, catalysis, information technologies, renewable energy production, renewable energy storage, ultrasensitive sensors, devices, materials, manufacturing, surfactants, and environmental applications. Basically, the development of green nanotechnology is generating interest in researchers toward eco-friendly, safe, and non-toxic routes of synthesis that can be used for manufacturing at a large scale. This is a simple, cost-effective, stable for long time, and reproducible aqueous room temperature synthesis method to obtain a self-assembly of gold nanoparticles.

2. Literature survey

Generally, colloidal gold is a kind of sol or colloidal suspension, which is called nanoparticles of gold in a water fluid. Colloidal gold nanoparticles usually show either an intense red or blue/purple color. Molecular sensors are generally composed of two main elements: a recognition unit, which selectively interacts with the molecule or ion to be detected, and a signaling unit that is responsible of generating a macroscopically measurable signal (optical, electrochemical, or mechanical) upon the molecular recognition event. In general, the term chemosensor is used when the binding between the receptor and the target analyte is

reversible and probe, when the recognition event takes place through an irreversible chemical reaction. The transduction mechanism, which is the mechanism by which the chemical interaction between the analyte and the recognition unit is converted into a change in the macroscopic signal of the signaling unit, will depend on the type of signaling unit and the structure of the receptor. The use of chemosensors for the selective colorimetric detection of small biologically active molecules offers some advantages over traditional instrumental analytical methods. Chromogenic probes are usually cheap and easy to use, and they do not require expensive instrumentation; very often, the presence of the analyte can be detected by the naked eye, which allows for rapid in-situ detection. Among the different approaches for colorimetric sensing, the use of gold nanoparticles (AuNPs) as scaffolds and signaling units for the construction of molecular sensors has attracted enormous interest for several reasons: they can be easily synthesized from Au(III) salts in various sizes and shapes. Their surface can be functionalized with a wide range of thiol- or disulfide-terminated organic ligands, by ligand exchange reactions, through the formation of strong Au—S bonds, leading to stable colloidal suspensions in water or organic solvents (depending on the ligand). Finally, gold nanoparticles have remarkable optoelectronic properties. In particular, the localized surface plasmon resonance (SPR) is influenced by not only the size and shape of nanoparticles but also by the dielectric properties of the environment and the proximity of other nanoparticles [1, 2]. Among the neurotransmitters, biogenic selective amines are paid specific attention due to their influence in areas ranging from biomarkers of specific problems or diseases [3–5] to quality control of foodstuffs [6, 7]. Nitric oxide (NO) is also a very important neurotransmitter in the central, peripheral, and enteric nervous systems (ENS) [8, 9]. Dopamine, the simplest biogenic catecholamine (CA), is an important neurotransmitter of the central and peripheral nervous systems [10]. An approach for the colorimetric detection of dopamine has been developed using 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole functionalized AuNPs. Dopamine induced the aggregation of the AuNPs through hydrogen bonding interactions [11]. Each dopamine molecule has three H-donor groups able to form hydrogen bonds (the amino and both hydroxyl groups). The recent rise in international apprehension over the use of chemical warfare (CW) agents in different conflictive scenarios has resulted in an increasing attention in the determination of these lethal chemicals. Among CW species, nerve agents are greatly treacherous, and their high toxicity and easy construction underscore the need to detect these deadly chemicals via quick and reliable procedures. AuNPs have been used as sensors for some nerve agent simulants with good results. Different sensing mechanisms have been used for detecting these compounds; for example, compensation of charges has been applied for this process [12]. The design sensing protocol takes advantage of the nucleophilic reactivity of pyridine moieties toward nerve gases [13].

Here, scattering interactions are more common for higher energy neutron spectra. Due to the large difference in mass between neutrons and gold nuclei, neutrons undergoing elastic scattering interactions (i.e., ballistic collisions) only transfer approximately 1% of their energy to the nucleus [14]. Inelastic scattering interactions, though less common, can transfer significantly more energy, leaving the nucleus in an excited state that results in gamma ray production. With sufficiently energetic incident neutrons, both scattering mechanisms are capable of generating gold primary knock-on atoms and generating displacement damage in the material microstructure. Radiation therapy is likely one of the most notable examples in which gold nanoparticle injections in the vicinity of a tumor or conjugated to antibodies such that they preferentially bind to cancer cells have been shown to increase

the local radiation dose during X-ray irradiation through secondary photon interactions, thus lessening the absorbed dose in the surrounding healthy tissue [15–17]. A similar local dose enhancement effect has been shown for proton and heavy-ion irradiation therapies, which are being pursued to further reduce the dose to healthy tissue as a consequence of how energetic charged particles deposit a majority of their energy at the end of their range [18, 19]. Furthermore, potential applications in satellites or space electronics would involve bombardment with high-energy cosmic radiation [20, 21].

On the other hand, ionizing radiation is known to have the ability to drastically alter the microstructure and performance of materials primarily through the displacement of constituent atoms from their lattice sites, resulting in the generation of damage and point defects [22]. These point defects tend to diffuse and coalesce into larger, ordered defect structures such as dislocation loops, cavities, and stacking faults, typically resulting in deleterious effects in structural materials such as radiation-induced hardening and embrittlement or void swelling. Irradiation can also cause solute redistribution in alloys and composite materials, encouraging the precipitation of secondary phases or promoting localized corrosion, which has been utilized in metal, ceramics, and polymers to provide added functionality not previously possible [23–25]. The fundamental mechanisms of radiation damage and the subsequent effects on the properties and performance of materials have been and continue to be heavily studied in commonly used and candidate materials for nuclear reactors and extraterrestrial applications. The mechanism of radiation damage in materials with limited dimensions has been shown to be significantly different from bulk material behavior [26, 27]. Due to the prodigious surface-to-volume ratio of nanoparticles compared to even thinner films, they have emerged as an attractive material choice for many applications. However, this same surface-to-volume ratio results in sputtering and free surface effects ultimately dominating the radiation response [28, 29]. Put simply, instead of diffusing into organized defect structures, the generated point defects tend to annihilate at the particle surface, or the material is ejected from the particle volume, as a result of the energetic collision [30, 31]. This can drastically alter the shape of individual particles and cause agglomeration of closely-spaced particle groupings [32–34]. Such morphological changes have the potential to adversely affect their efficacy in applications where the high surface-to-volume ratio and local structure are essential for performance.

The three primary interactions of photons with matter include the photoelectric effect, Compton scattering, and pair production [35]. In a photoelectric event, a photon completely transfers its energy to an orbital electron, ejecting it from its shell and ionizing the atom. This is the dominant interaction mechanism for low-energy photons. In Compton scattering, an incident photon transfers a portion of its energy to an orbital electron, and both the electron and photon continue typically with different trajectories when compared to the incoming photon. This will be the dominant interaction mechanism for incident photons of intermediate energies. Finally, pair production dominates for high energy photons and can only occur for incident photons greater than 1.022 MeV. In pair production, a photon interacts with the electromagnetic field surrounding the atomic nucleus and transforms into an electron and a positron, with the total photon energy less than the remaining energy of the two particles (0.511 MeV each) being shared between them. It should be noted that for high photon energies ($> \sim 8$ MeV), photodisintegration can also occur, in which the incident photon causes the atom to emit one or more neutrons, potentially resulting in a radioactive isotope of gold [36]. Additionally, photon irradiation experiments involving gold nanoparticles are prevalent, as X-ray therapies for

cancer treatment are fairly common practice [37–39]. While these studies are predominantly focused on the biological effects in the vicinity of cancerous tissue, they highlight how photons interact with these high-atomic-number (high-Z) nanoparticles to deposit their energy locally. High energy photons are also expected to cause Frenkel pair displacement damage (i.e., vacancy and interstitial defect pairs), primarily through the energetic electrons that they tend to generate. However, the effects of these displacement effects on the long-term stability of nanoparticle structures, if any, have not been studied to our knowledge. Charged particles are common by-products of radioactive decay and nuclear reactions and are a primary component of cosmic radiation. Accelerators and ion beams are also common ion sources used in both research and industry. For example, ions are frequently used in radiation damage experiments to simulate material microstructures resulting from neutron radiation exposure in nuclear reactor environments primarily because they are much less costly and can achieve similar damaged microstructures in a fraction of time [40]. Accelerators also have a slew of other potential applications ranging from materials analysis (e.g., electron microscopes and Rutherford backscattering) to ion beam modification. Beta (electron or positron) radiation either incident on or produced in gold will primarily lose its energy via ionization and bremsstrahlung radiation. As mentioned in the introduction, bremsstrahlung radiation occurs due to electron acceleration from interaction with an atomic nucleus and results in the production of a photon of energy equivalent to the energy lost by the electron. This interaction is again Z-dependent and is quite common for high-Z materials like gold [41]. While displacement or knock-on damage resulting from electrons is commonly observed in transmission electron microscopy experiments [42], the significant difference in the masses of an electron and a gold nucleus requires electron energies in excess of 1.35 MeV to create a single Frenkel pair [43]. In many cases, the role of the electron beam in altering the nanoparticle stability during these studies is not a result of interaction with the gold atoms itself, but with the organic capping ligands, as a result, the stability of the gold nanoparticles to beta radiation is often dictated by the organic capping agent chosen [44]. Alpha particles are common products of radioactive decay for actinides and other heavy radioactive isotopes, but, along with protons, deuterons, and tritons, they can also result from and induce a number of different nuclear reactions. For example, irradiation of Au-197 with protons with energies of 4.5 MeV or higher can cause a (p, n) reaction resulting in the production of metastable Hg-197 m [45]. However, the threshold energies of these reactions for gold are, in most cases, sufficiently high and reaction cross sections sufficiently low that these types of interactions rarely occur in practical applications. More often, light ions will interact via ionization and through coulombic forces. Similar to the other types of interactions discussed, ionization has the potential to result in the emission of characteristic X-rays and other secondary radiation. Coulombic interactions with other atomic nuclei can tend to cause displacement damage, usually in the form of Frenkel pairs or small, isolated cascades.

In general, the response of nanostructured materials to radiation damage is still poorly understood [46]. Despite the limited understanding in the general field, free-standing gold nanoparticles (usually drop-cast onto carbon or SiN TEM grids) have been used as the model system for testing and validation of TEM with in-situ ion irradiation capabilities [47–49]. Expanding on the known enhanced sputtering rate observed in gold thin foils exposed to a range of noble

gas ions [50], it was later shown by Ilinov et al. that gold nanorods irradiated with 80 keV Xe demonstrated sputtering rates three orders of magnitude higher than those predicted by classical sputtering simulations [33]. This surprising set of results means that classical models and expectations no longer hold true when predicting the radiation response of gold nanoparticles. The response of both free-standing and embedded gold nanoparticles is drastically different from that of gold in bulk or thin-film morphologies and is highly dependent on the radiation environment, particle morphology, and surface conditions. Additional work is needed to elucidate the underlying physics governing the increased sputtering and other scaling effects observed in gold nanoparticles [32, 33, 51]. Without a detailed understanding of the mechanisms active when the displacement damage length scale of the radiation event approaches that of the size of the nanoparticle exposed, it will be challenging to employ gold nanoparticles in most radiation environments. If the significant enhancement of sputtering is inherent and cannot be overcome, then the application of gold nanoparticles subject to ionizing radiation may be limited to those environments that produce minimal dose or sputtering yields.

3. Conclusions

Gold nanoparticles have diverse properties compared to those of bigger particles, which can be exploited in a broad spectrum of fields such as in renewable energy, nanomedicine, catalysis, information technologies, energy production, energy storage, sensitive nanosensors, nanomaterials, manufacturing, and real-time environmental applications. Taking into account the interesting photo-physical properties of sensitive gold nanoparticles, their easy functionalization, the use of aqueous solutions, and the detection by the naked eye, it can be concluded that the red or blue signal will continue to be very present in the molecular sensing field. It is concluded that selective gold nanoparticles have been extensively used for the design of colorimetric sensors as well as probes due to their interesting photo-physical properties. The use of gold nanoparticles for the preparation of colorimetric sensors is a very active field. The changes in the color of colloidal gold nanoparticles in solution because of the change in the surface plasmon absorption band upon aggregation or disaggregation processes can be easily used to transform the molecular recognition event into a macroscopic measurable signal. This change from red to blue can be perceived by the naked eye allowing in this way cheap and easy detection of the target analytes. The initial studies that have been done to observe the radiation response of gold nanoparticles to charged particle irradiation indicate that a significant enhancement of sputtering yield is present. This enhanced sputtering leads to the rapid disintegration of the original nanoparticle and the formation of unique satellite nanoscale arrangements as well as neurotransmitters, nerve agents, pesticides, and carboxylates of biological interest. The sensitivity and selectivity of the gold nanoparticle-based sensors toward the different bio- or chemical analytes will depend on the detection as well as recognition properties of the selective molecules attached to the surface of the low-dimensional nanoparticles. In this book, a selection of optically as well as biologically active molecules have been considered as analytes in broad interest such as photocatalysis, electrocatalysis, plasma-absorption, neurotransmitters, nerve agents, pesticides, and carboxylates.

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