



Review: Comparison of Gold Nanoparticle (AuNP) Synthesis Method

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Abstract

Gold nanoparticles (AuNP) have been analyzed as plasmonic materials for biomedical applications such as photothermal treatment agents for cancer and radiotherapy. The increasing demand for gold nanoparticles has led researchers to create more efficient, safe, and economical methods for industrial-scale production. The purpose of this paper aims to review the research results of scientific studies on the methods that can be used in synthesizing gold nanoparticles (AuNP) and determine the best method for the AuNP synthesis process on an industrial scale. This review contains 55 journals from 1996 to 2021 that discuss the AuNP synthesis method, along with the advantages and disadvantages of each method. Several methods can be used to synthesize AuNP, namely (1) chemical reduction, (2) biosynthesis, (3) sonochemistry, (4) laser ablation, (5) sputter deposition, and (6) irradiation- γ . The comparison results show that the best method for synthesizing AuNP is laser ablation because this method is relatively simple and effective for the formation of large amounts of nanoparticles. This review had a positive impact on the AuNP manufacturing industry in choosing the best method for synthesizing gold nanoparticles (AuNP).

Keywords: Synthesis Method, AuNP, Nanomaterial, Bottom-up, Top-down

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1. Introduction

Nanoparticles are materials that are smaller than 100 nm and have superior physicochemical properties compared to materials with a larger size (bulk) [1]. Unique optical properties, catalytic properties, electromagnetic properties, and bactericidal properties are some of the properties that only noble metals

have in the nano state and not in the bulk state. Gold nanoparticles (AuNP) are used in various industrial fields, such as the food and environmental industries, electronics, sensors, optics, catalysts, analytical chemistry, improvement of antibacterial strategies, DNA detection, genetic engineering, as well as in the health sector in drug delivery systems, drugs, antimicrobials, anticancer, disease diagnosis, and clinical treatment [2]. This is because gold particles have chemical stability, non-cytotoxicity, and biocompatibility properties, experience strong optical resonance in the visible light range, are sensitive to changes in the environment, size, and shape of the particles, and experience an increase in the local field of light interacting with the resonance system. The properties and applications of AuNP may vary based on the assembly and interactions between the particles [3,4]. The properties needed in the application of AuNP can be produced by scientists by controlling the nanoparticle structure, specific size, and size distribution of nanoparticles [1,5].

Based on these properties, the use of AuNP for commercial and industrial applications is increasing, so its availability must be increased and the synthesis method used must be modified to produce a more stable AuNP [6]. Many physical and chemical methods including top-down and bottom-up techniques have been developed to synthesize AuNP [2]. The top-down technique is carried out by breaking large materials into nanometer-sized particles. While the bottom-up technique is done by combining atoms, molecules, or clusters to form nanometer-sized particles. Synthesis by the physical method does not involve chemical reactions, but synthesis by the chemical method involves chemical reactions in the material and produces new materials with a nanometer size [7]. AuNP can be synthesized in various forms such as nanorods, nano triangles, nano prisms, and hexagonal platelets [4].

This review aims to compare several methods and materials to synthesize AuNP that we reviewed from 55 journals from 1996 to 2021. The methods we reviewed were chemical reduction [8], biosynthesis [2], sonochemistry [9], laser ablation [10], sputter deposition [11], irradiation- γ [12]. This review has a positive impact on the AuNP manufacturing industry in choosing the best method to synthesize AuNP. A comparison of methods for the synthesis of Gold Nanomaterials is presented in **Table 1**.

Table 1. Methods, results, advantages, and disadvantages of AuNP synthesis

Method	Material	Result	Advantages	Disadvantages	Ref
Chemical Reduction	Sugar (Sucrose), H ₂ AuCl ₄	Produces 10 nm AuNP	Cheap, safe, and environmentally friendly.	Need another stabilizer	[8,19]
	Alkohol, H ₂ AuCl ₄	Produces 5-12 nm AuNP	Serves for the manufacture of intelligent devices in biomedical sciences as diagnostic tools.	Using polyvinylpyrrolidone (PVP) is substance a dangerous.	[16-18]

	HAuCl ₄ , Trisodium Citrate	Produces 10-20 nm AuNP	Produces spherical nanoparticles with high monodispersity and expandable particle size range.	Using chemicals that are harmful to biosystems and the environment	[16,21]
	(Teknik Brust) Natrium borohidrida, NaBH ₄ , HAuCl ₄	Produces 1.5– 5.2 nm AuNP	Thermally stable AuNP Synthesis and produces air-stable AuNP with controlled size and low dispersion.	Using hazardous reducing agents for biosystems and the environment	[18,21]
	HAuCl ₄ , Ascorbic acid (Seed-mediated Growth)	Produces AuNP with a diameter of 5 nm - 40 nm	Simple, fast, and inexpensive process.	Using chemicals that are harmful to biosystems and the environment	[8,22]
Biosynthesis	Banana peel waste	Produces AuNP measuring about 300 nm	Less energy, simple, economical, safe, and non-toxic process.		[2,4,25],
Sonochemical	NaAuCl ₄ solution containing chitosan powder	Produces 22 nm AuNP	Produces pure crystals, effective process, monodispersed and very stable nanoparticles, and fast to produce nanomaterials.	The result is low, energy inefficient	[9,29-34],
Laser Ablation	Gold plate in toluene	Produces 0.9 nm AuNP	Simple and effective	Nanoparticles can block laser entry if the laser ablation time is long enough	[10, 13]
Sputter Deposition	1-ethyl-3-methylimidazolium tetrafluoroborate EMI-BF ₄ dan N,N,N-trimethyl-N-propylammonium bistrifluoromethanes	AuNP on EMI-BF ₄ resulted in an average diameter of d_{av} 5.5 nm by the standard deviation of 0.86 nm, while the sputter deposition to TMPA-TFSI	Simple and stable	Often the nanoparticles formed were less than 1 nm in size so they could not be detected with the TEM	[11,44]

	ulfonylimide TMPA-TFSI	resulted in the formation of smaller AuNP with d_{av} 1.9 nm and 0.46 nm			
Irradiasi- γ	HAuCl ₄	The average size of AuNP is 27, 12, and 7 nm, for solutions irradiated at 5, 10, and 15 kGy	AuNP yield is high, AuNP size is easy to control.	The AuNP stability evaluation stage was quite long, the absorption spectrum of the sample was recorded after 45 days	[12,14-15,50]

2. Materials and methods

The literature was searched through the Google Scholar site using a combination of the following keywords: synthesis method, AuNP, nanomaterial. The search results related to the research topic were downloaded as many as 90 articles. Furthermore, the article was read for the suitability of the title, abstract, and content screening where 39 articles were removed and the remaining 51 articles would be read in their entirety of content and data. Several methods and materials to synthesize AuNP were reviewed from 51 journals from 1996 to 2021. Some of the AuNP synthesis methods were chemical reduction, biosynthesis, sonochemistry, laser ablation, sputter deposition, and gamma-wave irradiation.

3. Results and discussion

3.1 Chemical Reduction

The chemical reduction method is a synthesis method of AuNP by reducing HAuCl₄ solution using an excess reducing agent. Commonly used reducing agents include Sodium Citrate, NH₂NH₂, Sodium Borohydride (NaBH₄), glucose, polysaccharides, alcohols, aldehydes, organic acids, and ethylene glycol [4,16]. The function of reducing agents is to reduce gold metal ions, followed by nucleation, and finally leads to the formation of metal nanoparticles [8]. Stabilizing agents added during the synthesis process can help the growth of nanoparticles and also protect the nanoparticles from the formation of agglomerations that can cause macro-sized particles. Stabilizers are generally also strong reducing agents [4].

Panigrahi et al. [8] conducted experiments for the synthesis of various metal nanoparticles (Au, Ag, Pt, Pd) using commonly available sugars, such as glucose, fructose, and sucrose as reducing agents. Ayyappan et al. [17] carried out an experiment on the synthesis of AuNP using an alcohol reducing agent

under reflux conditions. Verma et al. [18] carried out an experiment to synthesize AuNP by reducing Au^{3+} (HAuCl_4) to Au^0 using trisodium citrate, which also functions as a stabilizer.

3.1.1 Sucrose

Synthesis AuNP using sucrose as a reducing agent is a simple and safe AuNP synthesis method, this method produces AuNP with a diameter of about 20 nm [19]. The mechanism of the synthesis begins with the hydrolysis of sucrose by concentrated HAuCl_4 under the heating condition to produce glucose and fructose which were able to reduce the metal salts into metal particles [20]. Panigrahi et al. [8] synthesized AuNP using sucrose by dissolving 0.2 grams of sugar in 3.9 mL of water, then adding 10 microliters of HAuCl_4 10^{-2} M. The solution was heated in a water bath at a temperature of 70-75°C so that the color of the solution turned pink. Heating continued until the solution evaporated for 2 hours and dried, then added 4 mL of water to the solution to allow sonication for 30 minutes.

This process is highly reproducible, straightforward, and surfactant-free. Bio-friendly reagents are used for synthesis. In addition, only by changing the sugar and evaporating the precursor solution can achieve control of the particle size of the metal nanoparticles. Another important point is that the evolved particles can be stored for months in a desiccator without damaging the particle morphology and therefore can be used whenever needed [8].

3.1.2 Alcohols

Synthesis of AuNP using alcohol reducing agents. Then, polyvinylpyrrolidone (PVP) was used as a stabilizing agent and to control the formation of metal colloids. The starting material for the synthesis of AuNP is 0.1 g of chloroauric acid, the material is put into a container containing 100 ml of anhydrous ethanol which already contains a certain amount of polyvinylpyrrolidone (PVP) so that the material is soluble in alcohol. The ratio by weight of the metal salt to PVP is generally 1: 5 or 1: 10. The ethanol solution containing the metal salt and PVP is refluxed (~ 360 K) while stirring for 12 hours. This procedure was successful in producing AuNP, but it was necessary to add one equivalent of powdered magnesium metal to facilitate reduction. Mg metal acts as a reducing agent. Ethanol itself is oxidized to acetaldehyde and other products in the reaction [18].

3.1.3 Trisodium Citrate / Turkevich Method

The Turkevich method is one of the most famous techniques for the synthesis of AuNP which was first discovered in 1951, with the principle involving the reduction of gold ions (Au^{3+}) to gold atoms (Au^0) in the presence of reducing agents such as citrate in water, amino acids, ascorbic acid or UV light [21]. Verma et al. [18] synthesized AuNP using a solution of tetrachloroauric acid at several concentrations.

The beaker containing the tetrachloroauric acid solution was heated on a hot plate until it reached a temperature of 97°C while stirring with a magnetic stirrer. Furthermore, 1.5% trisodium citrate is added to the boiling solution periodically and quickly, accompanied by stirring until the solution changes color from light yellow to wine red [22].

The size of the nanoparticles and their distribution can be adjusted by changing the concentration of gold salt, trisodium citrate, temperature, and mixing speed. Frens [23] has modified the Turkevich method by varying the ratio of reducing agents and stabilizers. A high concentration of citrate can stabilize AuNP faster to produce AuNP with smaller sizes, while lower concentrations of citrate will cause the aggregation of small particles to become larger particles [3].

3.1.4 Brust Method

The Brust method was first described in 1994. This method is a two-phase process to produce AuNP of 1.5 nm – 5.2 nm in size using organic solvents and by varying the thiol to gold ratio [21]. This method allows an easy approach for the synthesis of thermally stable and air-stable AuNP with controlled size and low dispersion [22]. This method involves the transfer of a gold salt from an aqueous solution to an organic solvent (e.g. toluene) using a phase transfer agent (e.g., tetraoctyl ammonium bromide (TOAB)), and the gold is reduced by sodium borohydride, NaBH₄, then stabilized by alkanethiol resulting in a color change reaction from orange to brown indicating the formation of AuNP. Purification of AuNP was stabilized with dodecanethiol from TOAB [21].

3.1.5 Seed-mediated Growth Method

This method is the most preferred method for obtaining AuNP in shapes other than rods, cubes, and tubes [21]. The difference between this method and other methods is the addition of seeds in the synthesis process which is useful for controlling variations in the size and shape of nanoparticles during the AuNP synthesis process [7]. Seed particles are produced by the reduction of gold salts by strong reducing agents such as sodium borohydride [21]. In addition, it can also be done by mixing the 0.01 M HAuCl₄ 0.5 ml to 0.5 ml of trisodium citrate 0.01 M and 20 ml of pure water [7]. Furthermore, the seed particles were added to the metal salt solution in the presence of a weak reducing agent (ascorbic acid) and a structure regulating agent to prevent further nucleation and accelerate the anisotropic growth of AuNP. This method can synthesize AuNP with a diameter of 5 nm – 40 nm with a narrow size distribution. Particle size and geometry can be controlled by changing the ratio of metal salt concentration to seed concentration, reducing agents, and structural regulators [21-22].

3.2 Biosynthesis

Biosynthesis is a synthesis method by utilizing natural bioactive molecules that act as reducing agents, stabilizers, and capping agents. The bioactive content such as flavonoids, phenols, polyphenols, alkaloids, polysaccharides, terpenes, reducing sugars, ascorbic acid, and citric acid. These bioactive materials can reduce Au^{3+} ions to Au^0 by donating electrons [2,5]. AuNP biosynthesis can be carried out using extracts from plant tissues such as leaves, stems, fruits, bark, roots, bark, flowers, pulp, and juices or using microorganisms such as bacteria, yeasts, actinomycetes, fungi, etc [2,24]. Synthesis using biogenic agents (plants and microorganisms) is an environmentally friendly method, and this method only requires a short time to convert metal ions into nanoparticles [24].

One of the interesting studies related to AuNP biosynthesis is using banana peels [16,25]. The mechanism of biosynthesis using banana peels begins with washing the plant parts, washed with distilled water, and cut into small pieces [24]. Furthermore, extraction by the maceration method is done because it is easy and most commonly used for taking bioactive substances contained in plants. The extracts were further purified by different methods such as filtration and centrifugation [26,24]. Tetrachloroauric acid solution (HAuCl_4) was mixed with plant extracts using different ratios of gold salts and plant extracts, at room temperature. Its conversion into nanoparticles takes place for several minutes in one container [24]. The first conversion process is the reduction of Au^{3+} to Au^0 by bioactive content in plant extracts, which also acts as a stabilizer. AuNP stabilization was carried out by covering the outer surface of AuNP to prevent agglomeration [2]. A change in color during the synthesis indicates the process of excitation of plasmon nanoparticles, which causes the interaction of gold atoms in solution to form larger clusters (colloidal particles) [26]. The last step is to incubate the mixture to reduce the metal salts in it and observe the color changes that occur. Furthermore, the nanoparticles were separated from the mixture by centrifugation at high speed, then washed thoroughly in solvent/water and collected for further use [24].

3.3 Sonochemical

The principle of the sonication method is to utilize ultrasonic waves of very high frequency which are irradiated into the solution [27]. When a solution is irradiated with ultrasonic waves, collisions occur between the particles that make up the high-pressure solution. Su et al. [28] synthesized AuNP using the sonoelectrochemical method at cold temperatures. According to Jameel et al, the sonochemical method is an effective and fast method to produce nanomaterials [9]. In addition, sonochemical methods can replace conventional methods for synthesizing AuNP, because they can shorten the duration of preparation [29,30], resulting in pure crystals [31,32], highly stable monodispersions, and nanoparticles [33,34].

Okitsu et al. [35] synthesized AuNP using a sonochemical method using chitosan. Chitosan was washed with acetone, methanol, and water, then dried and sieved. Then chitosan powder with a size of <100 mesh was used in the study. A saturated solution of argon containing NaAuCl₄, propan-2-ol, and chitosan powder was sonicated in a cylindrical glass vessel. The formation of Au particles was sonochemically observed using a transmission electron microscope (TEM).

During irradiation, the chitosan powder was suspended in the solution and the color of the powder changed from white to purplish. After the reaction ends, the powder is separated by filtration and washed with water, then the suspension is dried. The colorless filtrate indicates that the Au(III) ions in the solution are completely reduced and the formation of Au particles (usually red or purple) is not left in the filtrate. In addition, a purplish-colored powder was obtained. These results suggest that the formation of Au particles is intact in the chitosan powder.

Fig 1 shows TEM analysis of AuNP on chitosan powder prepared from 1mM Au (III), 20 mM propan-2-ol, and 390 mg/L chitosan. The dark image is measured by electron diffraction based on the formation of Au particles. This proves that all Au particles are present on the chitosan surface and the average particle size measured is 22 nm. The formation of AuNP in chitosan can be assumed to follow 3 stages, namely: (1) reduction of Au (III) ions takes place by reducing the species formed by sonolysis of the water molecule propan-2-ol, (2) the formation of Au nuclei occurs rapidly to form AuNP in solution and (3) Au nanoparticles are adsorbed onto the chitosan surface. This means that chitosan powder acts as a stabilizer for AuNP so that it can suppress further growth of AuNP.

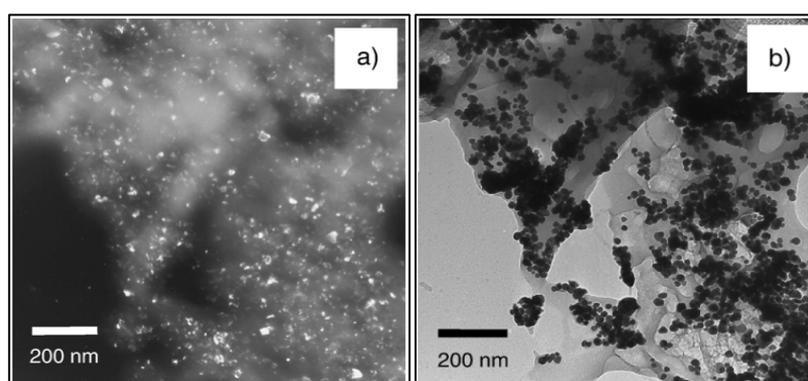


Fig 1. The results of the TEM analysis of AuNP contained in chitosan. a) Dark image; b) Bright image. The figure was adopted from Okitsu et al. [35].

3.4 Laser Ablation

In the laser ablation method, laser irradiation is used to reduce the particle size to nano size. The target solid is placed under a thin layer and then subjected to laser irradiation. Generally, Nd: YAG (neodymium-doped yttrium aluminum garnet) lasers with an output of 106 m, Ti: Sapphire (Titanium-doped sapphire) lasers, and copper vapor lasers are used [10]. Laser irradiation of the material causes

the fragmentation of the solid material in the form of nanoparticles, which remain in the liquid phase and surround the target resulting in a colloidal solution. The duration and energy of the laser determine the relative atomic number and ablation particles formed [37]. Several parameters such as duration of laser vibration, wavelength, ablation time, laser smoothness, and the effective surrounding liquid medium with or without surfactants can affect the ablation efficiency and the characteristics of the metal particles formed [38].

Amendola et al. [39] synthesized AuNP by laser ablation in toluene solution using an Nd: YAG laser at 1064 nm for 10 minutes with vibration of 9 ns at 10 Hz. The laser beam is focused using a 10 cm focal lens onto a point about 300 micrometers apart, on a gold plate at the bottom of the cell located 3 cm below the toluene. The solvent temperature was found to be less than 40 °C at the end of the synthesis. In general, nano-sized gold particles have a characteristic red color due to surface plasmon absorption (SPA) at 530 nm [40]. This also occurs when the laser ablation method is performed on dimethyl sulfoxide (DMSO) solution [41]. On the other hand, Amendola et al. [39] synthesized AuNP in toluene solution and produced AuNP without SPA characteristics. This also happened when AuNP was synthesized in an aromatic solution such as benzonitrile, in the absence of SPA. AuNP synthesis using toluene produces a yellowish solution rather than red. This is different from the results of the synthesis using other organic compounds with the same synthesis conditions. Fig 2 shows the UV-vis spectrum of the AuNP solution produced using the laser ablation method in several organic solutions.

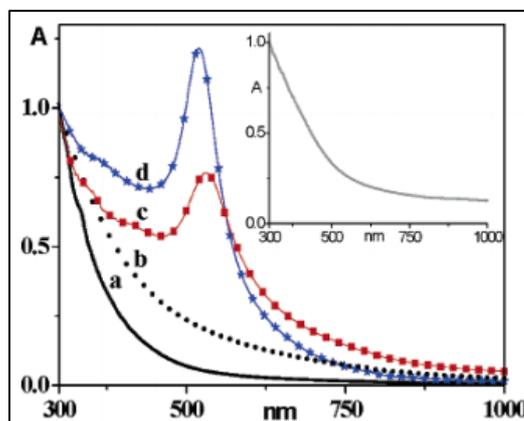


Fig 2. UV-vis spectra of AuNP solutions obtained by laser ablation in toluene (curve a, black line), in benzonitrile (curve b, dotted line), and for comparison, in DMSO (curve c, red squares) and in water (curve d, blue stars). The figure was adopted from Amendola et al. [39].

Based on TEM analysis, AuNP were surrounded by graphite nanocrystals of varying sizes up to tens of nanometers (Fig 3a). The graphite crystals are not observed around the nanoparticles, but the surface of these particles is not well visible. This indicates the presence of inclusions in the amorphous carbon matrix that affects the formation, although the distance between the particles is very small. Statistical

analysis of more than 1000 AuNP showed that the mean radius of the particles was only 0.9 nm, with a standard deviation of ± 0.5 nm.

It was experimentally shown that, for very small AuNP with a radius below 1.0 nm, SPA is almost absent [42,43]. The obtained particle distribution (Fig 3b) shows that almost 70% of the particles have a radius below 1.0 nm, the absence of SPA can be explained by considering that the carbon matrix hinders the formation of larger particles and causes the absence of SPA.

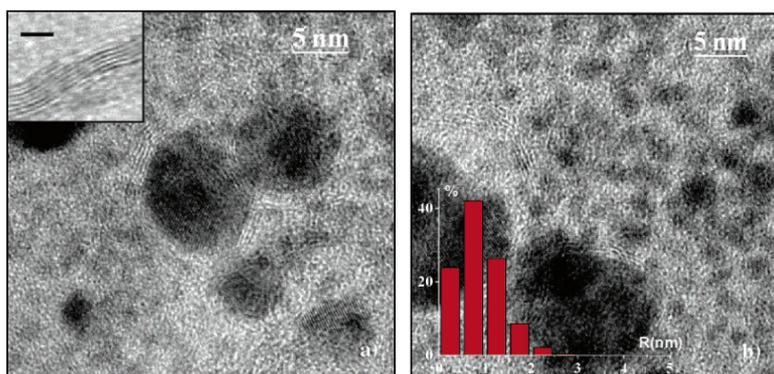


Fig 3. TEM images of AuNP included in a graphitic carbon matrix, (a) Planes of graphitic nanostructures surrounding AuNP; (b) Distribution of AuNP in the carbon matrix. The figure was adopted from Amendola et al. [39].

3.5 Sputter Deposition

Metal sputter deposition in the capture medium with very low vapor pressure is a simple and suitable method for producing metal nanoparticles (NPs) without chemical reactions [11], this method is also very clean and stable without the addition of reducing agents and stabilizers [44]. Careful selection of the capture medium and the temperature of the deposition media can control the size of the NPs produced. The sputtering condition also plays an important role in determining the size of the NP [11]. The size and size distribution of AuNP is strongly influenced by the temperature of the capture medium. This is because the change in temperature causes a drastic change in the viscosity of the medium and consequently affects the diffusion speed of the sputtered particles [11]. In addition, other important factors to determine the size and size distribution of NPs are sputtering conditions such as working distance between the target and capture medium, sputtering time, target temperature, applied voltage, discharge current, and gas pressure.

Fig 4 shows a temperature-regulated water circulation device. Then mounted to the bottom of the deposition chamber and in the target area in the sputter coater, this water circulation device keeps the temperature of the capture medium constant and at the target serves to maintain a constant target temperature [11].

Ionic Liquid (IL) of 1-ethyl-3-methylimidazolium tetrafluoroborate EMI-BF₄ and N, N, N-trimethyl-N-propylammonium bistrifluoromethanesulfonylimide TPA-TFSI was purchased from Kanto Chemical Co., Inc., and dried for 3 hours at 378 K under vacuum. An IL of 0.60 cm³ was leveled on a 20 cm² glass plate mounted horizontally in the sputter coater Eiko, IB-3. Then, it was placed at a distance of 35 mm from the target foil with 99.99% gold purity. Sputter deposition into the ILS was carried out with a current of about 4.0 mA under an air pressure of about 20 Pa at room temperature. The structure and size distribution of the nanoparticles were investigated using a JEOL 2010 TEM transmission electron microscope operated at an acceleration voltage of 120 kV. TEM samples were prepared by placing the IL solution onto a copper TEM lattice with an amorphous carbon layer, followed by the removal of any excess solution with filter paper [45].

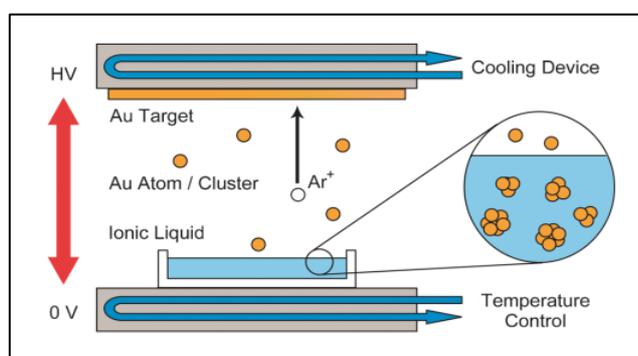


Fig 4. Schematic of the sputtering tool. The figure was adopted from Alvarez et al. [46]

Fig 5a shows the change in the absorption spectrum of EMI-BF₄ with the deposition of the Au sputter. The spectrum shows an onset of about 800 nm and a shoulder of about 520 nm assigned to the SPR peak of the AuNP surface plasmon resonance developed with the passage of sputtering time. The Au concentration in the IL was proportional to the sputtering time (**Fig 5a**). It is known that the SPR peak becomes very sharp with an increase in the size of the spherical AuNP from 2 to 9 nm [46]. However, the shape of the spectral peaks shown in **Fig 5a** appears to be unchanged even when the Au concentration reaches 33 mmol dm⁻³ after 120 min of sputtering. This indicates that successive sputtering did not cause a significant change in the size or size distribution of AuNP. Therefore, the desired AuNP concentration was obtained only by adjusting the sputtering time.

The colorless solutions of TPA-TFSI and EMI-BF₄ turn yellow and dark red, respectively, after sputter deposition of Au inset (**Fig 5b**), and their absorption spectra are highly dependent on the type of IL used. Sputtering Au to TPA-TFSI gives an absorption spectrum showing an onset of around 500 nm and an absorption shoulder of about 320 nm, which appears to be blue-shifted compared to the nanoparticle spectra in EMI-BF₄. Based on the previous research, if AuNP were synthesized by the Au

ion chemical reduction method, the SPR peak of 520 nm would disappear when the particle size was less than 2 nm [46]. In contrast, absorption peaks in the range of 300-450 nm were observed in the spectrum of the synthesized Au cluster [47]. This fact indicates that the sputtering method will be useful even for the preparation of metal clusters. The nanoparticles dispersed in both ILs were very stable and no recognizable changes in their absorption spectra were observed for several months under an N₂ atmosphere in the dark.

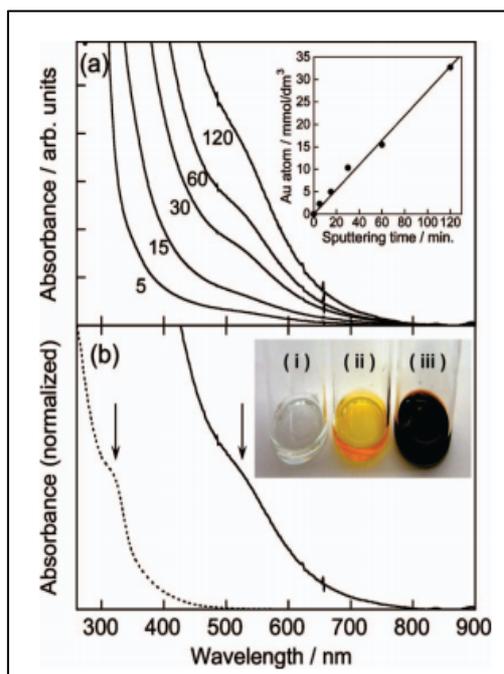


Fig 5. (a) Changes in EMI-BF₄ absorption spectrum with Au sputter deposition. (b) Normal absorption spectra of solid line EMI-BF₄ and dashed line TMPA-TFSI. The figure was adopted from Torimoto et al. [45].

The size distribution of AuNP was determined by measuring the size of individual particles in TEM images of more than 100 particles. **Fig 6a** shows that AuNP in EMI-BF₄ has an average diameter of 5.5 nm with a standard deviation of 0.86 nm, while the sputter deposition to TMPA-TFSI produces the formation of a much smaller AuNP with d_{av} of 1.9 nm and 0.46 nm. In recent studies, several nanoparticles incorporation during TEM observations should give d_{av} a larger value. The dependence of size variation on IL type in the TEM images roughly agrees with what would be expected from the absorption spectra in **Fig 6b**, although the exact crystal shape could not be determined in the current observations of Au groups in TFSI TMPA. Torimoto et al. [45] stated that in sputter deposition, the surface bombardment of Au foil with energetic gas ions causes the physical ejection of surface atoms or small Au clusters. Although the sputtered species are assumed to undergo fewer gas-phase collisions in the space between the Au foil and the IL solution due to the low gas pressure, their injection into the IL solution can create concentrations high enough to combine, resulting in the formation of larger particles.

Metal nanoparticles formed by chemical reduction have been reported to be stable in ILs even in the absence of an additional stabilizer, where the high dispersibility of nanoparticles is associated with the prevention of coalescence between particles both by strong adsorption of IL species on the surface and by electrostatic repulsion between the resulting particles [48].

The existence of these facts can be considered that the incorporation of species will continue to occur until the AuNP are stabilized by the adsorption of IL ions; degrees depending on the type of IL. Furthermore, it is known that the TFSI anions make coordination bonds with metal ions [49]. If this coordination ability works for its adsorption on the surface of nanoparticles, it is expected that strong TFSI adsorption will suppress the growth and/or coalescence of the particles.

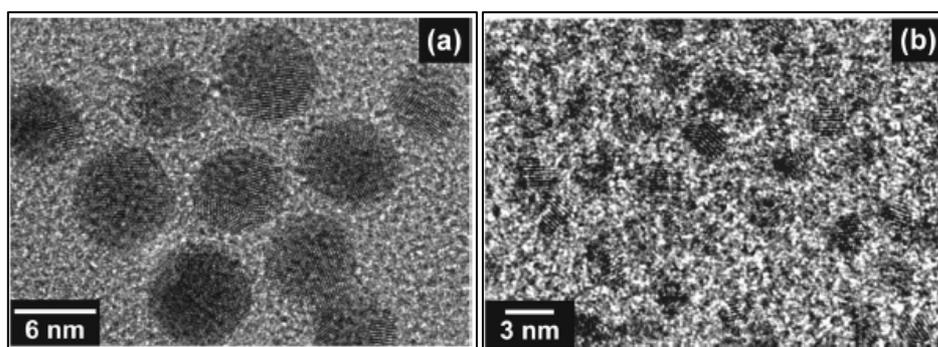


Fig 6. TEM of AuNP prepared by sputter deposition to (a) EMI-BF₄ and (b) TMPA-TFSI. The figure was adopted from Torimoto et al. [45].

3.6 Irradiation- γ

Prior to the experiment, a 10 mM HAuCl₄ mother liquor was prepared by dissolving the salt in distilled water. A mother liquor of 3 g L⁻¹ of chitosan (0.015 mol L⁻¹ in glucosamine units (GLA)) was prepared by dissolving the required amount of polymer in 1% acetic acid (pH-3.5). The presence of poor solubility of chitosan causes the mixture to be left overnight until a clear solution is obtained. A number of samples were prepared by mixing 0.5 ml of HAuCl₄ solution and the volume of the chitosan solution was varied. The final volume was adjusted to 5 ml with the addition of distilled water. Some samples were cleaned with Argon before irradiation. Samples were processed EB with an accelerator (10 MeV– 20 kW) at Ionisos (Chaumesnil-France), the irradiation dose varied between 5 and 50 kGy followed by 5 kGy or 25 kGy per cycle. The average radiation dose rate is 15 kGy/s, with a frequency of 500 Hz. The time interval between two successive irradiation cycles is equal to 5 minutes. Irradiation was carried out at VINAGAMMA Center (Ho Chi Minh City, Vietnam) on a 60Co cobalt source with a radiation rate of 1.1 kGy/hour and measured by the ethanol-chlorobenzene dosimetry system (ISO/ASTM 51538-2002(E)). After irradiation, the samples were stored at room temperature for 24 hours before analysis [50]. All samples were diluted 10 times before analysis. The optical path used was 1 cm. Au

nanoparticles (AuNP) were prepared by γ -irradiation with the total absorbed dose ranging from 7.8 and 23.4 kGy.

After irradiation, the initially colorless solution turned pink, the UV-visible spectrum showed an absorption band around 520 nm. This absorption is characteristic of the surface plasmon resonance phenomenon exhibited by AuNP (Fig 7). When compared with the spectrum of the unirradiated solution, the observed increase in absorbance at 260 and 285 nm, gradually increasing for higher radiation doses, was ascribed to the absorption carbonyl group formed under irradiation after chain cleavage by the H abstraction reaction [51]. Fig 7 shows that all Au (III) was reduced at a dose of 7.8 kGy because no effect was observed on the absorbance of the peak plasmon with higher doses. Under these conditions, the molar extinction coefficient per Au⁰ atom was determined to be 2400 dm³mol⁻¹cm⁻¹. The particle size obtained from the DLS measurements was 4.2 nm. This indicates that no effect can be observed on the absorption spectrum when the chitosan concentration varies in the [GLA]/[Au] ratio from 10 to 60, at a constant initial Au concentration. To evaluate the stability of AuNP, the absorption spectra of the samples were recorded after 45 days. The results showed that no significant changes were observed in the spectrum, meaning that the AuNP was stable over a long period. The absence of aggregation phenomena over such a period could be an important asset when considering the potential use of this type of nanoparticle for various applications.

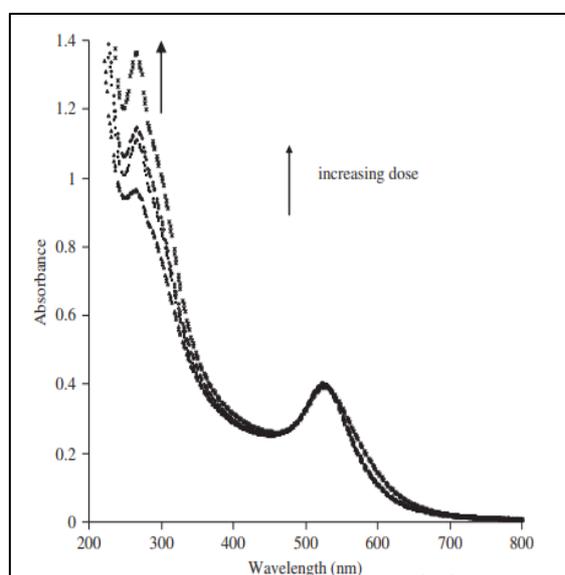


Fig 7. UV-vis spectra of AuNP prepared by γ -irradiation at doses of 7.8 kGy, 11.7 kGy, 15.6 kGy, 23.4 kGy. [HAuCl₄]¹/₄1 mM [CTS]¹/₄0.48%. The figure was adopted from Nguyen et al. [50].

Conclusion

Several methods can be used to synthesize AuNP, such as (1) Chemical reduction, (2) Biosynthesis, (3) Sonochemistry, (4) Laser Ablation, (5) Sputter deposition, and (6) irradiation- γ . Among these several

methods, the laser ablation method is the best because the technique used is relatively simple and effective for the formation of large amounts of nanoparticles. In addition, the characteristics of the nanoparticles can be changed by selecting the appropriate laser and liquid and the formation of nanoparticles can be carried out without adding surfactants to the liquid.

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