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Review of Synthesis and Functionalization of Gold Nanobipyramids

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ABSTRACT

Nanoparticles, as one of the nanotechnology implementations, have a potential application due to their advantages compared to bulk size. The type of nanoparticle widely used for many applications such as sensing, imaging, photothermal therapy and optical devices is a metal nanoparticle through their properties. The advantages of metal nanoparticles are unique plasmonic properties, size and shape control flexibility, low toxicity and the ability to be functionalized with other substances. Besides silver and platinum, gold become the most popular in recent decades because it is highly stable and does not quickly oxidize or corrode. Also, gold nanoparticles have a high extinction coefficient and efficient energy transfer properties, so they can enhance the detection signals, resulting in increased sensitivity and lower detection limits. Then gold nanoparticles are also biocompatible in the biomedical field. Several researchers successfully synthesize gold nanoparticles with different shapes for various applications using bottom-up methods, i.e., chemical reduction, electrochemical deposition, sol-gel and seed-mediated growth and top-down methods, i.e., mechanical milling, laser ablation, lithography, template-assisted synthesis, high-energy ball milling and plasma-based techniques. But, gold with a bipyramid shape is rarely reported, causing limited literature sources that discuss gold nanobipyramids (GNBPs). GNBPs have a stronger electric field enhancement than other shapes, so GNBPs are highly sensitive to surrounding medium change marked with the high value of Refractive Index Sensitivity (RIS) and Figure of Merit (FOM). Therefore, GNBPs have excellent potential to be implemented in various fields. This work discusses and overviews the synthesis method to produce GNBPs for further application. GNBPs can be fabricated through a synthesis process using microwave-assisted, one-pot, galvanic replacement and seed-mediated growth, with seed-mediated growth being the popular method. Then, GNBPs can be functionalized with several substances such as polymers, biomolecules, amine and thiol to bind with specific targeted analytes. Hence, due to their plasmonic properties, GNBPs are promising materials for many fields, especially sensing applications.

Keywords:
Gold nanobipyramids; gold nanoparticles; metal nanoparticles; functionalization

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1. Introduction

Nanoparticles, one of the nanotechnology implementations, have become increasingly popular in recent years. This is because nanoparticles have a significantly higher surface area than bulk materials due to their small size [1]. The increases in surface area lead to greater interaction with the surrounding environment, improving reactivity in sensing, catalysis and adsorption [2]. Also, nanoparticles' properties can be adjusted by controlling their size [3]. Materials at the nano size exhibit unique properties, such as quantum confinement, surface plasmon resonance and optical, electrical and magnetic properties [4]. Nanoparticles require lower quantities of materials than bulk materials, leading to efficient use of resources [5]. They can also support greener and more sustainable processes [6].

Metal nanoparticles become widely used compared to other forms of nanoparticles due to their plasmonic properties. Plasmons are collective oscillations of free electrons on metal surfaces, which enhance light-matter interactions. Metal nanoparticles can strongly absorb and scatter light at specific wavelengths, making metal nanoparticles highly suitable for applications in sensing, imaging, photothermal therapy and optical devices [7]. Metal nanoparticles are also generally stable and chemically inert, making them ideal for various environments [8]. Moreover, certain metals such as gold and silver are biocompatible, making them suitable for biomedical applications [9,10]. They are also readily available commercially, making them easily accessible to researchers and industries. Metal nanoparticle costs have become more affordable over time, further contributing to their widespread use [11].

Many researchers have successfully synthesized metal nanoparticles, both noble and metal oxide, with different structures for many applications such as biomedical and healthcare [12], catalysis [13], electronics and optics [14], energy conversion and storage [15], environmental remediation [16], also sensing and detection [17]. Gold nanobipyramids, as one of the noble metal nanoparticles, are rarely studied compared to spherical and rod shapes. As a result, the discussion and dissemination of research findings related to gold nanobipyramids are more limited. Whereas gold nanobipyramids have sharp and elongated tips, resulting in a strong electromagnetic field confinement and leading to enhanced light-matter interactions and increased sensitivity to the surrounding medium through the high value of Refractive Index Sensitivity (RIS) and Figure of Merit (FOM) [18]. Then, gold nanobipyramids have a relatively large surface area compared to other nanoparticle shapes, such as spheres or rods. The increased surface area provides more active sites for interactions with the surrounding medium. This allows for greater adsorption of target molecules or analytes onto the nanobipyramids surface, resulting in a stronger signal response [19]. Hence, this review discussed the synthesis method to produce gold nanobipyramids as sensing material focuses using several methods such as microwave-assisted, one-pot, galvanic replacement and seed-mediated growth. This work also reported about the functionalization process using polymers, biomolecules, amine and thiol on the gold nanobipyramids surface due to their specific targeted analyte binding.

2. Metal Nanoparticles

Metal nanoparticles are tiny particles of metal, typically with sizes ranging from a few to several hundred nanometres. They are composed of metal atoms arranged in a crystalline or amorphous structure. The unique properties of metal nanoparticles arise from their small size and high surface-to-volume ratio, which result in distinctive physical, chemical and optical characteristics compared to their bulk counterparts [20]. Nanoparticles exhibit a quantum confinement phenomenon, the confinement of electrons and their energy levels within small dimensions [21].

In recent decades, metal nanoparticles have been excellent candidates for several fields. When illuminated with light, metal nanoparticles can absorb and scatter light at specific wavelengths, which is highly sensitive to changes in the local environment. This sensitivity makes them ideal for detecting analytes and monitoring molecular interactions [22]. Besides, metal nanoparticles have a high surface-to-volume ratio due to their small size. This increased surface area provides more sites for analyte interactions, enhancing nanoparticle sensitivity [14]. They also exhibit low toxicity and can be functionalized with biomolecules for specific applications.

The typical metal nanoparticle widely used as a sensing material in the sensor system is a metal oxide and noble metal. Metal oxide nanoparticles are metal atoms combined with oxygen atoms to form an oxide compound [23]. Metal oxides can be derived from a wide range of metals, such as titanium (Ti), zinc (Zn), iron (Fe) and copper (Cu). Metal oxides are widely used, mostly as sensing materials. For example, a study by Pereira-Silva *et al.,* [24] reported the investigations through a Localized Surface Plasmon Resonance sensor using TiO_2-Au to detect biotin conjugated with horseradish peroxidase (HRP). They also used streptavidin as a receptor and coated it in the sensor system. Another research is reported by Wang *et al.,* [25] that conducted the detection of water pollutant p-cresol using ZnO and immobilized. He *et al.,* [26] also used Fe_2O_3 as a metal oxide sensing material for glucose detection. They modify Fe_2O_3 by adding the $Ni(OH)_2$ layer to improve the performance because $Ni(OH)_2$ has high electrocatalytic activity. Then, Proença *et al.,* [27] used CuO as a sensing material for carbon monoxide detection at room temperature. They modify with the implantation of Au to improve the system sensitivity.

Meanwhile, noble metal nanoparticles refer to nanoparticles composed of noble metals, which include gold (Au), silver (Ag), platinum (Pt) and palladium (Pd). These metals are classified as noble due to their resistance to oxidation and corrosion and relatively low reactivity [12]. Several observations are reported due to the usage of the noble metal, especially as a sensing material, such as research by Huang *et al.,* [28] that observed the detection of mercury(III) using gold with a spherical shape. The detection method they used was colorimetric determination. Chen *et al.,* [29] also used noble nanoparticles as sensing material through silver nanoparticles to detect phosmet residues in Oolong tea by surface-enhanced Raman scattering. Another application of noble metal is platinum nanoparticles supported by graphite/gelatine hydrogel to detect H_2O_2 by electrochemical detection method. This research is reported by Thirumalraj *et al.,* [30]. Yi *et al.,* [31] also reported their study through chloramphenicol detection by an electrochemical method using palladium nanoparticles as the sensing material. They decorated the palladium with graphene oxide to increase the electrochemical characteristics.

3. Gold Nanoparticles

Even though other noble metals such as silver, platinum and palladium also possess unique properties, gold nanoparticles are commonly used as sensing material. This condition is based on their advantageous properties, such as exhibiting a strong and tuneable absorption peak in the visible to the near-infrared region and allowing for easy detection and quantification of target analytes through changes in the nanoparticle's optical response [32]. Then, gold nanoparticles are highly stable and do not quickly oxidize or corrode. This stability ensures the longevity and reliability of the sensing platform. In addition, due to their high extinction coefficient and efficient energy transfer properties, gold nanoparticles can enhance the detection signals, resulting in increased sensitivity and lower detection limits [33]. Generally, the method used to synthesize gold nanoparticles is bottom-up and top-down.

Bottom-up approaches, which include chemical reduction, electrochemical deposition, sol-gel synthesis and seed-mediated growth, are ways to create nanoparticles by assembling them from smaller parts or atoms [34]. In the chemical reduction process, gold ions in a solution are reduced by a reducing agent, such as sodium citrate or sodium borohydride. The reduction process produces gold nanoparticles with certain diameters [35]. A gold electrode is submerged in a solution containing gold ions during the electrochemical deposition process and an electric current is then supplied to cause the reduction of the gold ions and the deposition of gold nanoparticles on the electrode surface [36]. The sol-gel process then entails the creation of a gold ion-containing sol-gel precursor solution, followed by gelation and drying. The dried gel is then calcined to obtain gold nanoparticles embedded in a solid matrix [37]. Moreover, the seed-mediated growth method involves synthesizing smaller gold nanoparticles (seeds) using a reducing agent. These seed nanoparticles then serve as nucleation sites for the further growth of gold atoms, resulting in larger nanoparticles with controlled shapes and sizes [38].

Besides that, top-down methods physically manipulate and reduce bulk gold materials to obtain nanoparticles, such as mechanical milling, laser ablation, lithography, template-assisted synthesis, high-energy ball milling and plasma-based techniques [34]. In mechanical milling, bulk gold materials are subjected to mechanical forces, such as milling, grinding or attrition, to break them down into smaller particles and obtain gold nanoparticles [39]. In the laser ablation method, a high-energy laser is focused on a target material containing gold, leading to vaporization and subsequent condensation. The condensed particles form gold nanoparticles [40]. Then, the lithography method is used to pattern or mask bulk gold films or surfaces. Subsequent etching or deposition processes selectively remove or deposit gold, forming gold nanoparticles with desired shapes and sizes [32]. Next, template-assisted synthesis involves using templates or moulds, such as porous materials, self-assembled monolayers or polymer matrices, to shape the synthesis of gold nanoparticles. The template guides the growth or deposition of gold, resulting in the desired nanoparticle structure [41]. In high-energy ball milling, high-energy collisions between balls and bulk gold materials cause mechanical deformation, fracturing and size reduction to produce gold nanoparticles. Furthermore, plasma-based techniques, such as plasma etching or sputtering, can selectively remove or deposit gold on surfaces, forming gold nanoparticles [42].

The shape and symmetry of gold nanoparticles can be broadly categorized into two types, i.e., isotropic and anisotropic. Isotropic nanoparticles refer to those with a symmetrical shape, where all dimensions are roughly the same. They exhibit a spherical or near-spherical shape. Bottom-up techniques, such as chemical reduction, are frequently used to create isotropic gold nanoparticles, where the reaction conditions are carefully managed to produce consistent particle sizes. Gold nanoparticles with a spherical shape have a high degree of symmetry and are frequently employed [43]. On the other hand, anisotropic nanoparticles are asymmetric or non-spherical in form and have differing dimensions along various axes. The structures of anisotropic gold nanoparticles might include rods, wires, plates, prisms or bipyramids. These structures are created using various synthesis techniques, including chemical etching, template-assisted synthesis and seed-mediated growth. The anisotropic form has distinct optical, electrical and catalytic capabilities compared to spherical nanoparticles. Anisotropic gold nanoparticles are widely sought-after for numerous applications, particularly sensing platforms, due to their distinctive features [44].

4. Gold Nanobipyramids

Anisotropic gold nanoparticles with bipyramidal structures are known as gold nanobipyramids (GNBPs). They are elongated nanoparticles with a bipyramid-like centre body and two pointed extremities. Typically, the triangle faces are broader and bigger, while the pointed ends are tapered and thinner. They have ten (111) triangular faces and 5-fold symmetry, with five triangle faces on top and down [45]. The illustration of GNBPs is shown in Figure 1, with length denoted as L and width designated as W. In addition, another parameter, i.e., aspect ratio, is the ratio between length and width [46].

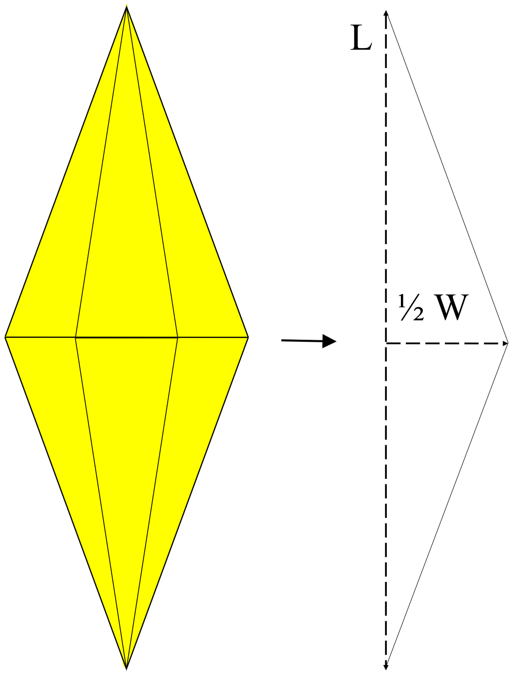

Fig. 1. The illustration of GNBPs

GNBP has a sharper Longitudinal Surface Plasmon Resonance (l-SPR) peak in the Localized Surface Plasmon Resonance (LSPR) spectrum, resulting in greater electric field enhancement than other forms. Figure 2 shows the LSPR spectrum of GNBPs.

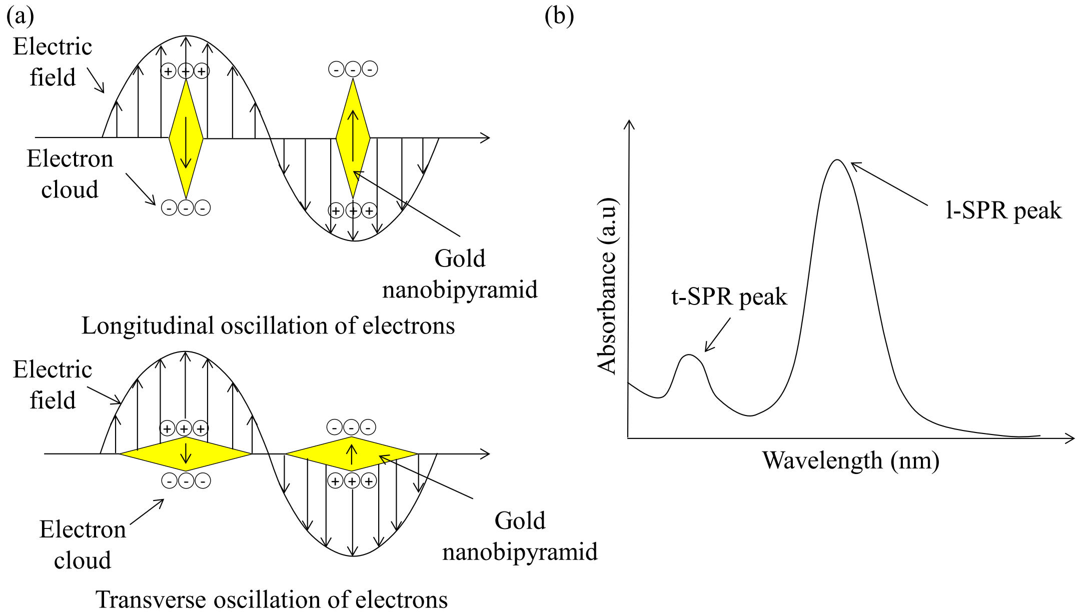

Fig. 2. LSPR phenomenon by GNBPs with (a) the direction of the oscillation (b) the LSPR spectrum

Figure 3 shows the electric field enhancement of GNBPs compared to rod shape. It can be seen that GNBPs have higher electric field enhancement due to their sharp tips. The increasing electric field enhancement can lead to an increasing LSPR phenomenon, resulting in a higher sensitivity to surrounding medium change through FOM and RIS value. According to the study by Nafisah *et al.*, [19] GNBPs have a sensitivity factor of 4.76 and 5.17 times larger than rod and bone rod shapes when applied for glyphosate detection.

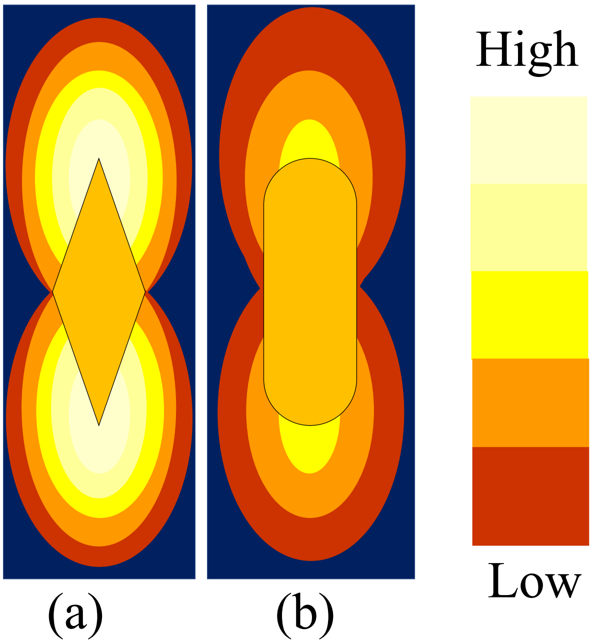

Fig. 3. Schematic of electric field enhancement of (a) bipyramid (b) rod shapes

4.1 Synthesis

Several methods can synthesize GNBPs, including microwave-assisted, one-pot, galvanic replacement and seed-mediated growth. In the microwave-assisted process, microwave radiation is used to heat the reaction mixture, accelerating the development of GNBPs. The advantage of this method is that the GNBPs results are uniform [47]. Several studies conducted this synthesis method, such as Huynh *et al.,* [48] using microwave irradiation and applying GNBPs in immunosensors for chloramphenicol residual detection. They embedded the GNBPs in a quartz crystal microbalance system. Another research by Mendoza *et al.,* [49] used this method to synthesize GNBPs with core-shell structure, then used to generate singlet oxygen. On the other hand, this method is also used to produce Au supported by ZnO in a hexagonal pyramid shape and is utilized in solar energy conversion [50].

The one-pot method is a simplified approach that involves the simultaneous formation of the GNBPs in a single reaction mixture. This method eliminates the need for separate seed synthesis and growth steps, making the process more convenient and efficient [51]. However, researchers rarely use this method due to several drawbacks, such as hardness to control size and shape through fast time reaction, lack of reproducibility, unsuitable for large-scale production and limited tunability because it is not easily controllable [52]. This method was successfully implemented in gold nanorod production, i.e., a study by Okitsu *et al.,* [53] with a length of < 50 nm, a study by Lai *et al.,* [54] with a length of 88 nm and a study by Abidi *et al.,* [55] with a diameter of 10 – 15 nm. Another structure produced by this method is nanoworms that show good performances as photothermal bactericidal in *Escherichia coli* and *Staphylococcus aureus* by Liao *et al.,* [56].

The galvanic replacement method uses a sacrificial template with the desired shape, such as silver nanoprisms or gold nanorods. The template is immersed in a gold precursor solution and a suitable reducing agent is added. As a result, the gold ions from the precursor deposit onto the template surface, replacing the original material and forming GNBPs [57]. In the study reported by Xu *et al.,* [58] the galvanic replacement method is used in purification and etching processes. GNBPs are produced embedded with Ag-Pt hollow nanostructure. In the study by Yip *et al.,* [59] they make GNBPs coated with Ag and then use this method to replace Ag with Pd to exhibit larger responses for hydrogen detection. Zhuo *et al.,* [60] also use this method to replace the GNBPs-coated Ag nanorod with a hollow nanostructure.

Moreover, in the seed-mediated growth method, gold nanomaterial of a specific size and shape, called seeds, are first synthesized using a particular process, such as the citrate reduction process [61]. Then, the GNBPs are grown from these seeds by adding a reducing agent, such as ascorbic acid, gold precursor solution, chloroauric acid, the presence of a surfactant and cetyltrimethylammonium bromide [46]. So, the size and shape of the nanobipyramids are controlled in the growth process.

Seed-mediated growth method is often used to synthesize GNBPs because it offers a high degree of control over the nanoparticles' size, shape and optical properties. Additionally, the seed-mediated growth method can produce GNBPs with high yield and reproducibility, making them reliable for large-scale production. The method also allows for fine-tuning the plasmonic properties of the nanobipyramids, such as their absorption and scattering spectra, by controlling the aspect ratio and other structural parameters [62]. Several studies have reported, such as Ye *et al.*, [63] parameter research in silver nitrate, ascorbic acid and gold seed. Nafisah *et al.,* [46] also reported the synthesis of GNBPs using a seed-mediated growth method; the parameter is replacing hydrochloric acid with other acids. This method expands to the etching process in producing a monodisperse of GNBPs, reported by Li *et al.*, [64] with silver used in the etching process. An additional review of the synthesis process to produce GNBPs is shown in Table 1.

Table 1
Overview of synthesis method to produce GNBPs

Year	Author [ref]	Contribution	Remarks
2012	Guo *et al.,* [65]	Using electrolyte-induced electrostatic screening method to separate gold with spherical shape.	The purity obtained is above 90 %. The purity process is conducted by centrifuge growth solution. Then, the residue is dispersed using deionized water. After that, 1.5 M NaCl is added to the centrifuge process. The sample is dropped into a substrate and can be used further.
2013	Zhou *et al.,* [66]	Using nanoseed with different sizes, i.e., 49 nm, 37 nm, 33 nm and 25 nm.	The resulting GNBPs are as follows: 1) using 49 nm produces 220 nm in length and 60 nm in width; 2) using 37 nm produces 175 nm in length and 57 nm in width; 3) using 33 nm produces 157 nm in length and 47 in width and 4) using 25 nm produce 110 nm in the length and 36 nm in width.
2014	Liu *et al.,* [67]	Compare the circular dichroism response of GNBPs with other shapes.	The purification method is a centrifuge, increasing the yield from 30 % to 90 %. Then, the full width at the half-maximum value obtained is 50 nm.
2015	Li *et al.,* [64]	Focused on the purification of GNBPs with several sizes.	After synthesis, several steps are carried out for purification, i.e., Ag overgrowth, depletion-induced self-separation and chemical etching.
2016	Qi *et al.,* [68]	Varying HCl, $AgNO_3$, AA and seed solution volume	The optimum volume for HCl and AA is 40 µL, $AgNO_3$ is 50 µL and the seed solution is 10 µL.

2017	Kang *et al.,* [69]	Using CTBAB and Ag^+ as surfactants produces GNBPs modification in surface concave.	The value of near-field electric field enhancements improved 3.3 times higher than flat GNBPs in 1,064 nm excitation. The size reached 285 nm in length and 59 nm in diameter.
2018	Ngo *et al.,* [70]	Using CTAB as the surfactant and polyethylene glycol, polyvinyl alcohol and chitosan as the stabilizers.	Stabilized GNBPs can decrease the purity of spherical shape and produce GNBPs with lower intensity peaks and blue shift. The average size after stabilization is 81 ± 6 nm in length and 33 ± 3 nm in diameter.
2019	Chateau *et al.,* [62]	Using $HAuCl_4$ with higher concentration than usual, i.e., 15 mM and 8-hydroxyquinoline as reducing agents.	The seed solution produced is 120 mL, larger than usual in 8 – 20 mL. The growth solution is added to the overgrown seed and produces GNBPs with high purity and diameter in 10 nm.
2020	Ye *et al.,* [63]	Changing silver nitrate, ascorbic acid and gold seed flow rate.	The results show that optimum GNBPs produce a flow rate of 160 µL/min silver nitrate, gold seed and 120 µL/min ascorbic acid. In condition 160 µL/min silver nitrate, the length increases to 145 nm and the diameter increases to 48 nm. In condition 160 µL/min gold, the length and diameter were obtained at 104 nm and 34 nm. In condition 120 µL/min ascorbic acid, the length and diameter were obtained at 79 nm and 38 nm.
2021	Nafisah *et al.,* [46]	Using different acids in the growth process, i.e., HCl, H_2SO_4 and HF.	The optimum GNBPs yield was obtained in 0.6 mL HCl and H_2SO_4, while HF was 0.4 mL. HCl has significantly affected the length of GNBPs instead of the diameter. Meanwhile, H_2SO_4 affects both parameters, but the optimum length is obtained in 0.4 mL. HF produces longer GNBPs than other acids. The best aspect ratio was obtained using 0.4 mL of HCl.
2022	Ye *et al.,* [71]	The usage of CTAC and citric acid in the seeding process. Meanwhile, NADH is used instead of ascorbic acid in the growth process.	The extinction value is 0.4011, with a wavelength of 522 nm. Then, the GNBPs solution was deposited into a four-layer substrate for further application.

4.2 Functionalization

The functionalization process can occur on the GNBPs surface for several reasons. Functionalization, for instance, can improve GNBPs' stability and dispersibility in wide solvents or biological conditions. It makes it possible to better manage and manipulate the nanoparticles by preventing agglomeration or precipitation. Functionalization can then offer target molecules particular binding sites. This circumstance enables the targeted detection of certain analytes or target biomolecules, such as proteins, DNA or tiny molecules [72]. Functionalization can also be utilized to modify GNBPs' optical characteristics. Adding certain compounds to the nanoparticle surface may alter light absorption and scattering, which modifies the plasmonic resonance characteristics [73]. A ligand on the surface of the GNBPs is the result of the functionalization procedure, as seen in Figure 4. The functionalization agent might replace the CTA^+ layer with cetyltrimethylammonium bromide in the synthesis process, reducing toxicity [74]. Several substances can be used as functionalization agents for GNBPs, such as polymers, biomolecules, amine and thiol.

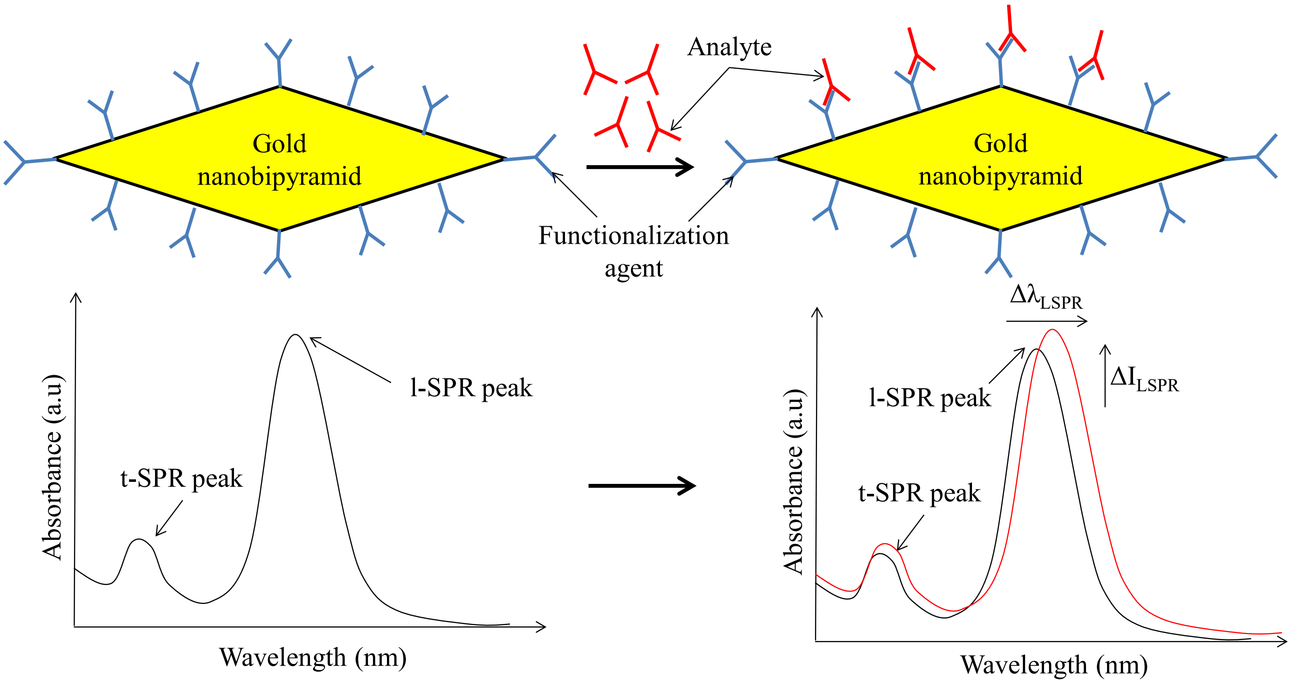

Fig. 4. The illustration of the functionalization agent on the GNBPs surface

Polymers can operate as a functionalization agent by providing receptive sites for attaching biomolecules like antibodies, proteins, DNA or enzymes. This enables specific targeting, bioconjugation and the creation of bioactive interfaces for various biomedical applications. Besides that, by modifying the surface properties of GNBPs with polymers, they can be readily dispersed in aqueous solutions or other organic solvents. Several studies have been successfully done through the usage of polymers. For example, a study by Liu *et al.,* [75] used polyethylene glycol (PEG) to functionalize the GNBPs surface and observed its effect on cancer cell ablation. Then another observation is also reported by Amirjani *et al.,* [76]. They use polyvinyl alcohol to functionalize GNBPs and then apply them in the photodynamic therapy of cancer. Stoia *et al.,* [77] also use the kind of polymer, i.e., polyethyleneimine, to functionalize GNBPs and control drug delivery in the human body.

Besides polymers, biomolecules can also be used as functionalization agents for GNBPs. Examples of biomolecules are proteins, peptides and nucleic acids. The study conducted by this functionalization agent is Wang *et al.,* [78]. They use DNAzyme to functionalize GNBPs and apply them to the *Vibrio parahaemolyticus* detection. Basically, biomolecule ligands are used in simple shapes, for example, spherical. Shi *et al.*, [79] research uses spherical DNA for miRNA detection in the exosome location. Li *et al.,* [80] also used biomolecules such as non-thiolated nucleic acid to detect kanamycin antibiotics. Lee *et al.,* [81] conducted the pRNA to functionalize gold with a spherical structure for microRNA detection. Mehranfar *et al.,* [82] reported their research on implementing peptides as a ligand and applying them for SARS-CoV-2 detection.

The usage of a functionalization agent depends on the analyte targeted. But amine and thiol groups become popular functionalization agents several researchers use because both can form strong covalent bonds with gold surfaces by forming gold-amine or gold-thiol complexes. These bonds are generally stable and resistant to degradation, ensuring the long-term stability of the functionalized GNBPs [83,84]. Furthermore, both amine and thiol can be easily modified with various molecules, such as biomolecules, polymers or dyes, introducing specific properties or functionalities to the GNBPs [85]. Then, amine and thiol are commonly found in biological systems, making them compatible with natural environments. The functionalization of GNBPs with amine or thiol groups can enhance their biocompatibility and minimize potential cytotoxicity [86]. According to their advantage as functionalization agents, amine and thiol are most widely used to detect glucose.

Amine groups (-NH_2) are primary functional groups that can form covalent bonds with glucose molecules through an imine formation or Schiff base reaction. This reaction involves the reaction between an aldehyde or ketone group on the glucose molecule with an amine group on the ligand. The resulting imine bond is stable and can detect glucose through changes in the plasmonic properties of the GNBPs [87]. On the other hand, thiol groups (-SH) can form disulfide bonds with glucose molecules, allowing for specific and selective detection of glucose through changes in the plasmonic properties of the GNBPs [88]. In addition, the overview of functionalization using amine and thiol in various nanomaterials for glucose detection is shown in Table 2 and Table 3.

Table 2
Overview of nanoparticle functionalization using amine to detect glucose

Year	Author [ref]	Nanoparticle	Functionalization Agent	Method of Detection	Remarks
2010	Li *et al.,* [89]	Organosilica nanosphere	3-(trimethoxysilyl) propyl methacrylate	Electrochemical	Nanocomposite immobilized using glucose oxidase. Then, the sensitivity reaches 122.6 $\mu AmM^{-1}cm^{-2\ and}$ the detection limit is 2 µM. This study uses a linear range of glucose in 0.006 – 1.3 mM.
2011	Tasviri *et al.,* [90]	TiO_2-CNTs	3-aminopropyl-triethoxysilane	Catalysis	The time response is obtained at 3 s. Also, the sensor's sensitivity is 0.007 µAM-1 with a detection range of up to 266 µM.
2012	Gu *et al.,* [91]	Graphene-nanoplates	Amine-terminated ionic liquid	Electrochemical	The linear range of glucose is 10 – 500 µM with a detection limit of 3.33 µM. The time detection needed is 30 minutes. The basal level obtained is 0.376 ± 0.028 mM.
2013	Zhang *et al.,* [92]	Graphene composite	Amine-terminated ionic liquid	Electrocatalysis	The minimum value of glucose that can be detected is 0.05 $mmolL^{-1}$. The linear response towards glucose is up to 8 $mmolL^{-1}$.
2014	Khodadadei *et al.,* [93]	Multiwalled CNTs	3-aminopropyl-triethoxysilane	Electrochemical	Glucose oxidase is immobilized in a glassy carbon electrode. The range used for glucose is 17 – 646 µM and the sensitivity reaches 12.3 $\mu A/mMcm^2$. The detection limit is 9 µM, with the Michaelis-Menten constant being 480 µM.
2015	Vasu *et al.,* [94]	Graphene oxide	N-(3-dimethylaminopropyl)-N-ethylcarbodiimde hydrochloride	FET devices	The variation of glucose concentration is 100 pM – 100 mM, with a limit of detection in 2 nM. Electrical conductance changes to 0.1 mM when it detects other analytes, i.e., lactose.
2016	Dabbawala *et al.,* [95]	Nanoporous polymer	Non-coordinating tertiary amine moieties	Catalytic hydrogenation	Ru supports the nanomaterial and the system's selectivity reaches 98 %.
2017	Wang *et al.,* [96]	$AgInS_2$ quantum dots	Polyethyleneimine	Photoluminescence	The nanomaterial is synthesized using an electric pressure cooker. The limit of detection is 0.9 µM, with a linear concentration between photoluminescence and glucose of 1 – 10 µM and 10 – 1,000 µM.

2018	Navaee *et al.*, [97]	Flavine adenine dinucleotide	Amino-Gr	Electrochemical	Sensitivity reached 0.177 $AM^{-1}cm^{-2\ \text{and}}$ the range of glucose used was 0.5 – 6.9 mM. In addition, the limit of detection of the system is 50 µM.
2019	Buk *et al.*, [98]	GNPs/CQDs	Cysteamine	Photocatalysis	Amine is used to functionalize GNPs before combining with CQDs. Then, the nanomaterial combination is immobilized using glucose oxidase. The sensitivity resulting from this system is 626.06 µA $mM^{-1}cm^{-2}$.
2019	Maity *et al.,* [99]	CNTs	Ethylenediamine	Electrochemical	After functionalization, CNTs are immobilized with glucose oxidase. The sensitivity is 246 $\mu AmM^{-1}cm^{-2}$ with a 1 – 10 mM detection range. The limit of detection is 63 µM.
2020	Ortega-Liebana *et al.,* [100]	GNPs-mesoporous silica	3-aminopropyltriethoxysilane	Catalysis	Nanomaterial is immobilized with electrostatic attraction using glucose oxidase. The limit of detection is 150 mM.
2021	Van Tam *et al.,* [101]	Graphene quantum dots	3-aminopropyltriethoxysilane	Fluorescent	Nanocomposite is synthesized using microwave-assisted pyrolysis of fructose. The detection limit is 2.1 µM and a linear response is obtained in 0 – 1 mM.
2022	Kaimal *et al.,* [102]	Graphene quantum dots – silica NPs	dopamine hydrochloride	Electrochemical	The glucose concentration range is 0.5 – 7 µM with a detection limit of 0.5 µM. The sensitivity was established in 2.64 $\mu A\mu M^{-1}$.

Based on Table 2 and Table 3, amine and thiol are commonly used as ligands for glucose detection, but no functionalized GNBPs exist. Hence, functionalization on the GNBPs is a promising sensing material that refers to the advantages of GNBPs compared to other structures.

Table 3
Overview of nanoparticle functionalization using thiol to detect glucose

Year	Author	Nanoparticle	Functionalization Agent	Method of Detection	Remarks
2007	Pandey *et al.,* [103]	GNPs	11-mercaptoundecanoic acid	Electrocatalysis	Glucose oxidase is used to immobilize the nanocomposite and the result affected is the increase of the Michaelis-Menten constant (from 3.74 mM to 5.85 mM). Also, the shelf life of this functionalized nanomaterial is 6 months due to controlling pH and temperature.
2011	Radhakumary *et al.,* [104]	GNPs	16-mercaptohexadecanoic acid	Visible colour change	Glucose oxidase is used in functionalized GNPs. Then, the solution's colour is changed from red to blue if glucose is detected in 100 µg/mL.
2012	Chen *et al.,* [105]	Gold nanoporous	5,5-dithiobis (2-nitrobenzoic acid)	Electrochemical	The role of thiol is to immobilize glucose oxidase enzymes on nanoporous surfaces. The limit of detection is 10 µM and the linear response is obtained in 3 – 8 mM.

2013	Vesali-Naseh *et al.,* [106]	GNPs-CNTs	5,5-dithiobis (2-nitrobenzoic acid)	Electrocatalysis	Glucose oxidase is used to immobilize nanocomposite in a hybrid way. The glucose concentration range used is 0.4 – 4 mM, with limit detection in 3 µM. Also, the sensitivity is obtained in 23.1 µAmM^{-1}cm^{-2}. It is crucial to control the pH 7 in the redox process when the hybrid way has occurred.
2014	Chowdhury *et al.,* [107]	gold-polyaniline nanocomposite	thiol-ended ssDNA	Electrochemical	This system used chronoamperometric and flow cell methods, with a biomolecule attached to glucose oxidase. The detection limit is 1 µM, with a sensitivity value of 14.63 µAmM^{-1}cm^{-2}. In addition, the glucose concentration range is 1 µM – 20 mM.
2015	Bas [108]	GNPs	4-aminothiophenol	Electrocatalysis	Thiol groups are mixed with graphene oxide to detect glucose. Liner range obtained in 0.1 – 3.8 mM with a sensitivity of 17.68 µAmM^{-1}cm^{-2}. Furthermore, the limit detection of glucose is 0.075 mM.
2016	Spampinato *et al.,* [109]	GNPs	1-ß-D-thio-glucose modification	Catalysis	The functionalization process works well on flat surfaces and affects the lower density.
2017	Hazra *et al.,* [110]	RuNPs	3-mercaptopropyl trimethoxysilane	Electrochemical	The electrode used is screen-printed Au. The glucose concentration range is 10 µM – 100 mM, with a detection limit of 1.67 µM (0.3 ppm).
2018	Nandwana *et al.,* [111]	Fe_3O_4/MoS_2 nanocomposite	11-mercaptoundecanoic acid	Absorbance	Fe_3O_4/MoS_2 nanocomposite has a higher catalysis effect than Fe_3O_4 nanoparticle and MoS_2 nanosheet. The limit of detection is 2.4 µM.
2019	Murugan *et al.,* [112]	GNPs-CNTs	Mercaptoacetic acid, mercaptopropionic acid and mercaptosuccinic acid	Electrochemical	GNPs average size is 14 nm using mercaptosuccinic acid. The glucose concentration range is 0.12 – 4 µM with limit detection in 0.036 µM. Also, the optimum potential applied in the system is 0.8 V/s.
2019	Akhtar *et al.,* [113]	Gold thin film	Thiol graphene	Electrochemical	The sensitivity is 3.1732 µAmM^{-1}cm^{-2}, with a detection limit of 0.3194 mM. The linear response is obtained in the 3 – 9 mM, with R^2 being 0.94693. The system is immobilized using 1-ethyl-3(3- (dimethylamino) propyl) carbodiimide.
2020	Baghayeri *et al.,* [114]	CuO honeycombs /AgNPs	triethoxypropylthiole	Electrochemical	The thiol solution is dropped into a carbon electrode and then nanomaterials are electrodeposited on the surface. The sensor is stable in 0.06 – 1,000 µM because it produces a linear response. Then, the limit of detection is 15 nM.

2021	Chen *et al.,* [115]	Carbon dots	mercaptopropylamine	Fluorescence	Glucose oxidase is used to support the catalytic oxidation process. The range of glucose that can be detected is 0.1 – 1,000 µM, with the limit detection of this device being 0.03 µM.
2022	Qian *et al.,* [116]	Graphene oxide/PEG/rhodamine B/gold nanocomposite	Dithiobis	Electrochemical	Nanographene oxide is a base for the thiol active side. The range of glucose used is 0.5 – 1 mM. In addition to glucose, $-0.295\ V$ it changes those values as operating potential points.

5. Summary and Future Prospective

GNBPs have higher sensitivity compared to other shapes. This condition gives GNBPs an excellent potential to be applied in many fields. GNBPs can be synthesized using microwave-assisted, one-pot, galvanic replacement and seed-mediated growth. Seed-mediated growth become a popular method that researchers widely use due to the advantages of a high degree of control over the nanoparticles' size, shape and optical properties. Also, using the seed-mediated growth method, GNBPs can be synthesized in large-scale production. Then, GNBPs can be functionalized using polymers, biomolecules, amine and thiol. The functionalization agent chosen depends on the specific bind to the targeted analyte. However, the researcher commonly uses amine and thiol because of their ability to produce solid covalent bonds on the GNBPs surfaces and they are primarily used to detect glucose analytes. Hence, GNBPs functionalized with amine and thiol become promising materials for sensing applications, especially in glucose detection. Further modification and development on the fabrication of GNBPs are needed to improve the sensing performances.

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