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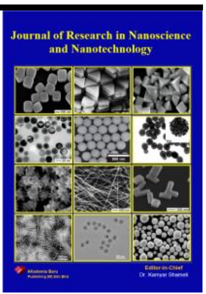

Green Synthesis of Gold Nanoparticles Based on Plant Extract for Nanofluid-based Hybrid Photovoltaic System Application

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ABSTRACT

Green synthesis technique has overcome the limitation of chemical and physical methods including cost, usage of toxic chemicals and hazardous by-products. Gold nanoparticles (Au-NPs) synthesized using green synthesis method have received great interest due to the physicochemical characteristics and their application in various fields. This review paper has reviewed the capability of various parts of the plant in order to act as green reducing agent to cap gold source to Au-NPs. This includes the root/rhizomes, bark, leaves, flowers, fruits and fruits peel. All previous works have successfully synthesized Au-NPs in nano-range and even with smaller size up to ~10 nm. Finally, this review paper has review current progress of nanofluid-based hybrid photovoltaic-system that used Au-NPs in the nanofluid due to their high surface plasmon resonance.

Keywords:
Gold nanoparticles, green synthesis, plant extract, solar energy harvesting

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1. Introduction

Gold has existed for million years ago and ancient peoples have exploited gold for various purposes especially in the field of diseases treatment. For instance, back in 1800s, ancient peoples believed that rheumatoid arthritis was curable, or possibly treatable by gold salts [1]. Even though gold has been used in a long time ago, but recent years have seen a rise in the number of research works related to Au-NPs due to their versatile properties [2]. These properties include facile synthesis, surface plasmon resonance, surface chemistry and multi-functionalization, high surface area to volume ratio and stable nature that has huge potential for advancement in multiple areas such as for solar energy harvesting [3], drug deliveries [4], anticancer treatment [5], antibacterial agent [6], immobilization [7] and sensors [8].

A. Balfourier et al reported that Au-NPs-based technologies are still in preclinical development, with only few translations to clinical trials [9]. This led researchers to investigate more sophisticated techniques for the synthesis of Au-NPs which will makes the future of Au-NPs become very promising. In general, the synthesis technique for Au-NPs is similar to the synthesis conditions of other nanoparticles [10]. There are two options for the classification of synthesis approach. First classification is according to the way of the synthesis i.e., top-down approach and bottom-up approach as per illustrated in Figure 1. In top-down approach, starting materials typically in micrometer, millimeter or centimeter size range are broken down using a variety of synthesis methods until nanometer range size. Most common examples of method in this approach are chemical etching, laser ablation, mechanical milling and sputtering. Meanwhile, in the bottom-up approach, starting materials are generally chemical reagents that are allowed to react in a variety of experimental conditions until the average size of the units formed by the assembly of atoms, molecules or ions is roughly as expected in the nano range [11]. Chemical vapor deposition (CVD), sol-gel processes, pyrolysis (laser and spray) and aerosol processes are the general example of bottom-up approach.

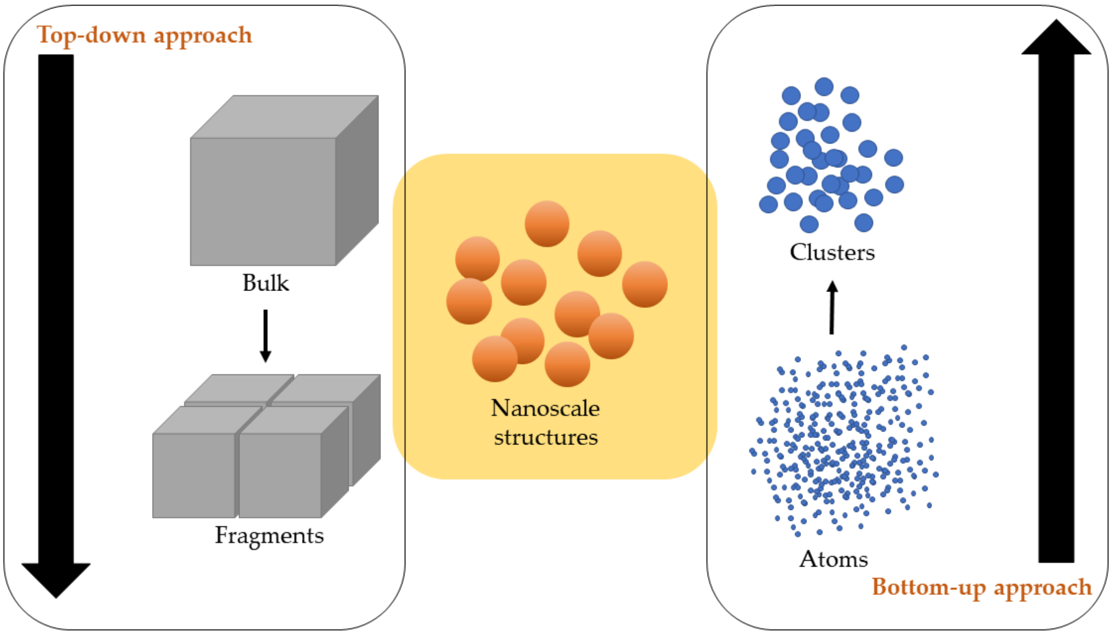

Figure 1. Top-down and bottom-up approaches to synthesis Au-NPs

Next classification involves the methodological approach i.e., chemical method, physical method and green method. Chemical synthesis method is also known as chemical reduction. There are two major steps to synthesis Au-NPs via this method [12]. First step refers to the use of reduction agents such as borohydrides, polyols, hydrogen peroxide and many others in which these chemicals provide electrons to reduce the gold ion, Au^{3+} and Au^{+} to Au-NPs state, Au^{0}. Chloroauric acid ($HAuCl_4$) with gold in its Au^{3+} oxidation state is the most common precursor choose by majority of researchers to produce Au-NPs [13-14]. Due to corrosive properties of $HAuCl_4$, it is important to take note that handling must not use any metal apparatus i.e., metal spatula. Subsequently, the second step in chemical reduction involves the use of stabilization agents such as citrate dihydrate, phosphorus ligands, polymers and surfactants. These chemicals work by stabilizing the Au-NPs against aggregation. It imputed a repulsive force that allows a controllable synthesis of Au-NPs in term of rate, final size and shape. Even though there are two steps involved in the chemical reduction method as explained in previous sentences, however in certain experiment, some chemicals play a double role as both reduction and stabilizing agents.

In chemical reduction, Turkevich method which was first introduced by Turkevich in 1951 is one of the most infamous method for the synthesis of Au-NPs [15]. This method is based on the reduction of $HAuCl_4$ by trisodium citrate dihydrate or also known as sodium citrate. Sodium citrate was rapidly added into boiling $HAuCl_4$ solution under vigorous stirring and solution color was changed from light yellow to wine red indicated the presence of Au-NPs [16-17]. Another method available in chemical reduction is The Brust-Schiffrin method. In 1994, Brust and Schiffrin discovered this method in which it allowed an easy approach to the synthesis of stable Au-NPs i.e., able to control the size and low dispersity. Generally, tetrachloroaurate ion ($AuCl_{4-}$) is used as the precursor and transferred to a toluene phase from an aqueous solution using tetraoctylammonium bromide (TOAB) as the phase-transfer agent. Later, it was reduced by sodium borohydride ($NaBH_4$) in the presence of dodecanethiol. The solution mixture color was change from orange to deep brown after the reduction agent was added. This clearly indicates the presence of Au-NPs [18].

Second method in the synthesis classification to produce Au-NPs is physical method that involve powerful irradiation such as microwave radiation, gamma radiation and photolithography and high energy technique such as radio frequency (RF) plasma method, high energy ball milling and ion sputtering. Physical methods are usually operated in high electrical energy thus leading to high operational cost. For instance, starting metal or precursor in RF plasma method was heated above its evaporation point using high voltage RF coils to generate a plasma that will be reacted with helium gas to form high temperature plasma [19]. Another example of high energy consumption can also be seen via ball milling method where the ball mills rotate with high energy inside a chamber to crush the solid starting metal into nano crystallites [20].

Over the years, plethora of research to synthesize Au-NPs in desired size, shape and stability have been successfully conducted in both of the aforementioned methods. It is also undeniable that many fascinating applications have been improved by Au-NPs fabricated via chemical and physical methods. Unfortunately, these methods are well-known in using hazardous and highly toxic chemicals which indirectly contributed to adverse health effects harmful to the nature [21]. In addition, the reducing and stabilizing agents used in chemical and physical synthesis methods to produce Au-NPs are expensive [22].

Thus, in the light of this issues, researchers have diverted their attention to more environmentally friendly green synthesis method to produce Au-NPs. Green synthesis method introduced non-toxic and non-hazardous reducing and stabilizing agents where it uses a plant phytochemicals or microbial enzymes to replace toxic agents in chemical and physical methods. It is safe, not harmful to the environment and economically viable due to no costly chemicals are used [23]. Moreover, plants and microbes were readily available and facile to tailor the size, shape and nature just by modifying its culture pH, temperature and nutrient media. In general, the phytochemicals in the plants and enzymes present in the microorganisms' act like a reducing agent and also as a stabilizing agent for Au-NPs [24]. A number of new results in the synthesis of Au-NPs using plant and microorganisms were presented from year to year and the improvement gained are clear. The principles of green chemistry have now become a reference guide for researchers, scientists, and chemist around the world for developing less hazardous chemical products and by-products. These principles include waste prevention, atom economy, less hazardous chemical synthesis, designing safer chemicals, safer solvents and auxiliaries, design for energy efficiency, use of renewable feed-stocks, reduce derivatives, catalysis, design for degradation, real-time pollution prevention and safer chemistry for accident prevention [25].

Post synthesis, Au-NPs can be further purified and characterized by using various characterization techniques such as ultraviolet–visible spectroscopy (UV-VIS), Fourier-transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and dynamic light scattering (DLS). However, Au-NPs need to undergo a sample preparation prior to the characterization. In general, there are different approaches available for the sample preparation. For instance, in SEM analysis it was reported that air-drying or critical-point drying (CPD) methods was suitable for the liquid-rich biological sample, while freeze drying method was more preferred for biological sample that contains less liquid [26]. An illustration of green synthesis technique of Au-NPs is illustrated in Figure 2.

Au-NPs has an interesting characteristics that applicable in multiple discipline [27]. Au-NPs have greater biological compatibility and able to provide microscopic probes for the study of the cancer cell, hence making it popular in the biomedical application [28-29]. Furthermore, Au-NPs can accumulate in the cancerous cell and show the cytotoxic effect of the specific cell and cell receptor. Meanwhile, high stability due to gold-sulphur bond and the optical properties like plasmon resonance having better exhibited by Au-NPs making it useful in solar energy harvesting application [30-31].

Therefore, in this review, detailed study will be focuses on the green synthesis of Au-NPs based on plant extract and it is hoped that this review will provide a holistic understanding of the green synthesis technique of Au-NPs and effectively give valuable insights into its utilization in nanofluid-based hybrid photovoltaic system application.

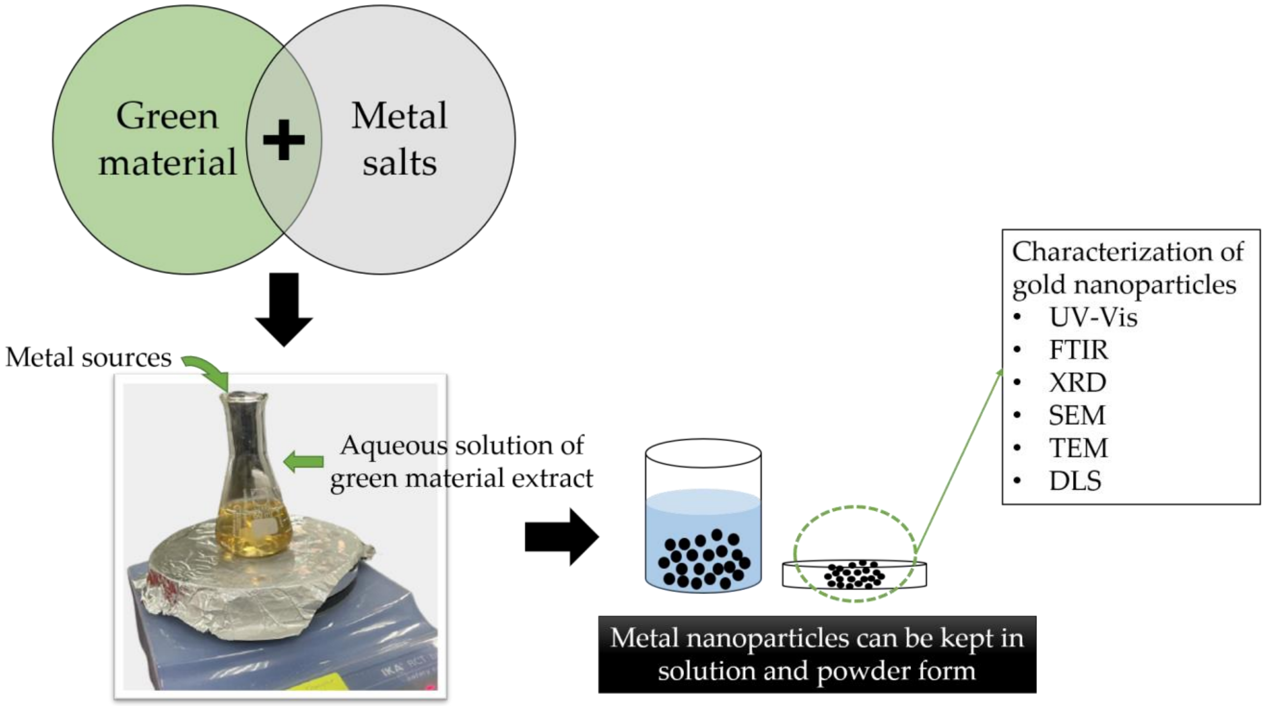

Figure 2. Illustration of green synthesis techniques of metal nanoparticles and its available characterization.

2. Green Synthesis of Gold Nanoparticles Based on Plant Extract

This section discusses the production of Au-NPs using green synthesis technique based on plant extract. Plants are some of the greenest materials available for Au-NPs synthesis due to the presence of many organic compounds which can act as reducing and stabilizing agents. Phenols, flavonoids, amino acids, carboxylic acids, ketones and proteins are some examples of reactive compounds in the plant. In Figure 3, every part of a plant can be utilized as a green material for the synthesis of Au-NPs.

Figure 3. Green materials can be found in every part of a plant and usable for the synthesis of Au-NPs

In green synthesis technique of Au-NPs, any part of the plant that will be used as a reducing agent will be processed to get its extract. The plant must be washed with distilled water prior to the extraction process in order to eliminate dirt. The extraction process consists of several steps starting from drying the plant, grinding it into powdered form, extraction, filtering the extract, concentrating the extract and finally drying the excess solvent in the extract. For Au-NPs synthesis, the variable parameters can be broadened from the concentration and ratio of gold salt and plant extract, time, temperature up to the pH level. The green synthesis technique is way simpler, where the extract is simply mixed with the gold salt in one pot and their conversion into Au-NPs will usually take place within minutes. The reduction of Au^{3+} to Au^0 can visually monitor by observing the colour change from yellow to purplish red indicating successful synthesis of Au-NPs. As the phytochemical from the plant is acting as a reducing and stabilizing agent, the external capping agents are no longer required and hence promoting more ecofriendly and cost-saving method. Lastly, high-speed centrifugation followed by washing thoroughly in solvent or water can be done in order to collect the Au-NPs for further use. The product of Au-NPs will be able to offer a stable-nanosized, environmentally friendly Au-NPs and serve as a potential competitor once they are commercialized however, the mass production of Au-NPs is remained limited due to the control over the size and stability. This is particularly when the physiochemical properties of Au-NPs are affected by the variable parameters and reaction environment. Huang *et al* in their work have explained that the reaction time can increased if the temperature is increased however, agglomeration of nanoparticle tends to happen which then will reduce the stability [32].

2.1 Green Synthesis of Gold Nanoparticle Based on Root and Rhizome

A number of studies have reported an instant production of Au-NPs by utilizing the root and rhizome of the plant. The results are interesting and help to justify the capability of this plant part as a reducing agent. Recent work that utilized the rhizome extract of *Rhodiola Rosea* have shown a successful production of stable and crystalline Au-NPs with average diameter of 13-17 nm. The flavonoids, terpenes and phenols were the bioactive compounds that have been detected on the Au-NPs surface which could be responsible for reducing the gold salt to Au-NPs and stabilizing them [33]. This has been extensively discussed in literature where the phytochemicals present in the plant parts serve the twin role of reducing agent besides being a stabilizer [34]. In another work, rhizome extract of *Anemarrhena Asphodeloides* was used to produce a spherical Au-NPs with diameter of 258 nm where phenolic compounds were also found to be responsible for the reduction of gold salt to Au-NPs and stabilizing the nanoparticle [35]. The green synthesis of spherical and stable Au-NPs with size of above 20 nm also has been experimentally demonstrated by Babu and colleagues using the rhizome of *Zingiber officinale* or its common name, ginger. It is apparent that the phytochemicals from the ginger has contributed in reducing the gold salts to Au-NPs and this formation of Au-NPs can be visually observed by the colour change reaction from colorless to purple [36].

Next, the green synthesis of Au-NPs by using the plant roots have also showed the similar trends as the rhizome. For example, a rapid production of spherical Au-NPs with crystallite sizes of 6 nm was synthesized by using the root extract of *Cibotium barometz* as the reducing agent and stabilizer [37]. This plant is popularly known as Gouji in Chinese herbal medicine are abundantly available in most of Southeast Asia country. It is reported that the root of this plant contained high flavonoid content such as kaempferol and onychin. Meanwhile, caffeic acid and protocatechuic acid are the phenolic acid available from this plant root. In this experimental work, aqueous root extract was obtained by adding 5 g of dried grounded powder of Gouji root into 100 mL distilled water and boiled for 30 min at 100 °C. The preparation of aqueous root extract in this research was environmentally safe as no chemicals involved in the process. Post synthesis of Au-NPs, the result from Fourier Transform Infrared (FTIR) spectroscopy showed that flavonoids, phenolic acids and fatty acids in Gouji root extract were responsible for the reduction of gold salts to Au-NPs. In another research, the root of medicinal plant named *Glycyrrhiza uralensis* or commonly known as Chinese liquorice was used to synthesize Au-NPs [38]. The presence of glycyrrhizin and flavonoids in this plant have contributed to its wide usage in the traditional medication for multiple treatment and hence contributed also as reducing agent to reduce the gold salts to Au-NPs in the synthesis process. Similar to [37], Huo et al also demonstrated a rapid and eco-friendly green synthesis of Au-NPs by using its root. In this experimental work, it was reported that Au-NPs has rapidly obtained within 4 mins at 80 °C and complete reaction did not require additional reducing and stabilizing agents.

To sum up this section, the results from all previous work in green synthesis of Au-NPs that utilizes rhizomes and root extract has been discussed and it has been demonstrated that the green reduction of gold salts ion to Au-NPs was assisted by the phytochemical compound in the rhizomes and roots extract.

2.2 Green Synthesis of Gold Nanoparticles Based on Bark

Bark is one of the most important part for woody plant. Previously, Omar and colleagues have successfully demonstrated an eco-friendly synthesis of spherical Au-NPs that utilizes cinnamon bark extract as a reducing agent and stabilizer [39]. Based on the result from transmission electron microscopy (TEM), it was found that the Au-NPs size distribution at around 35 nm. Similar work has also been pursued by others in which another non-toxic and eco-friendly synthesis of spherical Au-NPs have successfully produced by using the bark of *Terminalia Mantaly* or its common name is a Madagascar almond [40].

The reduction of gold ion, Au^{3+} and Au^{+} to Au-NPs state, Au^{0} has also successfully demonstrated by Leyla et al by using *Juglans regia L.* tree bark or also known as walnut. The reported synthesized colloidal Au-NPs was red purple color and results from this research has proven that the green synthesis method using bark as reducing agent is simple, environmentally friendly and well accessible method to produce Au-NPs [41]. Another research by Zahra et al also has utilized *Juglans regia* husk extract to synthesize Au-NPs. The synthesized has been performed in two different methods. The former is Au-NPs were synthesized at room temperature and the latter is Au-NPs were synthesized at moderate temperature that is 45°C. The research claimed that these two different methods were performed in order to study the effect of temperature on stirring times as well as the yield of reactions. From the TEM analysis, it was reported that Au-NPs formed a spherical shape with the mean diameter size were 19.19±4.7 nm at room temperature and 14.32±3.24 nm at moderate temperature has successfully synthesized by using *Juglans regia* husk extract [42].

2.3 Green Synthesis of Gold Nanoparticles Based on Leaves

Leaves are the plant part that always available and easier to obtain compared to other parts of the plant. A number of studies and reviews have been undertaken to explore the potential of leaves as reducing and stabilizing agent for the synthesis of Au-NPs. For example, in the field of medicine, many researches were interested in the medicinal leaves to synthesis Au-NPs due to the richness of their anti-oxidants compounds and phenolic compounds. The first study for green synthesis of Au-NPs was conducted by Shankar and his colleagues in 2003. They have been successfully synthesized a various shape of Au-NPs such as triangular, spherical, decahedral and icosahedral by using geranium leaves extract for the reducing and capping agent [43]. By carefully examining the report, it is found that terpenoids in the leaves extract was a responsible compound to reduce the gold salts ion to Au-NPs. Meanwhile, the latest work in green synthesis of Au-NPs was performed by leaves extract of *Populus Alba* in which the carbohydrates and polyphenols compound in its leaves were suggested as the possible reducing agent for reduction of gold salts ion to Au-NPs [44]. As the result, a uniform and stable Au-NPs was successfully synthesized with size range at 162 ± 41 nm. Next, smaller Au-NPs was reported by using the leaves extract of *Curcumae Kwangsiensis* [5]. The size of Au-NPs was measured by TEM and revealed the size range from 8-25 nm. The result supported by FESEM where the observed spherical Au-NPs has average size of 16.6 nm. Recent study by Mohamed Hosny *et al* has reported an instantaneous, cost-effective and environmentally friendly Au-NPs using aqueous extracts of *Persicaria Salicifolia* leaves [45]. The colloidal Au-NPs was violet in colour and mostly the shape was spherical as per observed using TEM analysis. The Au-NPs synthesized with this leaf extract was even smaller, that is in between 5 and 23 nm. The synthesized Au-NPs was then applied into an anti-cancer study and it showed that it has an outstanding anticancer efficiency with an IC50 of 2.2 µg/mL.

2.4 Green Synthesis of Gold Nanoparticles Based on Flower

Other than plant leaves, flowers were also popular among the researchers in order to become green reducing agent to reduce gold sources to Au-NPs. Generally, flowers are seen as something that useful to decorate homes, gardens and more. However, flowers have a much more benefit than decorating. It has different colour and each colour differs due to the pigmentation. Anthocyanins and carotenoids are the main sources for the flower coloration. For instance, carotenoids are the compound that responsible for yellows, oranges and reds. Recent research conducted by Fahad et al has successfully synthesized Au-NPs by using *Crocus Sativus* (saffron) flower and their antibacterial activities was studied [46]. The Au-NPs were characterized by UV-Vis spectroscopy, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD). Results yield the synthesize Au-NPs have size of 25-32 nm and the shape was spherical. Next, the method attempts to control the size of Au-NPs was demonstrated by Chan et al through the synthesis of Au-NPs using *Clitoria Ternatea* flower extract [22]. Most significant finding from the research is that Au-NPs size was affected by the reaction time for the production of the Au-NPs. The size range for Au-NPs has an average diameter in between 15.53±10.12 nm to 59.43±27.62 nm has been achieved from the research by varying the concentration of gold salts. There were clear benefits to be seen in research conducted by Anand and colleagues where they demonstrated a green synthesis of Au-NPs that is cost-effective, simple and quick by using agroforestry waste of *Moringa Oleifera* petals [47]. In this research, Au-NPs were studied for their catalytic reduction of nitrophenol and nitroaniline in which the result shown a rapid reduction. The synthesis of Au-NPs using *Moringa Oleifera* petals were stable with size of 5 nm in diameter. The shapes were triangular, hexagonal and nearly spherical in shape. To sum up this section, it can be seen that flowers have great advantages in order to act as green reducing agents to reduce gold sources to Au-NPs and previous researches reported a good formation and stable Au-NPs with smaller size.

2.5 Green Synthesis of Gold Nanoparticles Based on Fruit

For some plant, fruits are not always available all the time. However, it still received a huge attention among the researchers due to their high nutrition compounds which capable to capping gold sources to Au-NPs. Mohanan et al have reported the work on the green synthesis of Au-NPs based on Citrus fruits. *Citrus limon, citrus reticulate* and *citrus sinensis* were used in this work. Citrus fruit extract composed of a variety of phenolic acid, phenolic esters, flavonoids, triterpenoids, thiamine and mangiferin. Citrus fruit are found to be rich in citric acid and ascorbic acid that may be responsible for reduction of metal ions and efficient stabilization of synthesized nanoparticles. The study revealed that the size of Au-NPs synthesized with *Citrus limon, citrus reticulate* and *citrus sinensis* were 32.2 nm, 43.4 nm and 56.7 nm respectively. The morphology shapes of the Au-NPs were spherical for all the extracts. The phytochemicals of the fruit help in stabilizing and capping the Au-NPs. This supported by the recent work by A. Kureshi et al in which the Au-NPs were synthesized using two *Garcinia species* that is *Garcinia Indica* and *Garcinia Cambogia* fruit and SEM analysis showed spherical and triangular shape Au-NPs and their average sizes were ranging from 2 – 10 nm [48]. Results from XRD also showed that the Au-NPs were to be in good agreement with the particle size of 8 – 11 nm. As conclusion, A. Kureshi et al summarized that the synthesis method was simple and eco-friendly with phenolic compounds in the *Garcinia* species were contributed as the reduction agents. The summary of plant parts and their capability to act as the reducing agent in the green synthesis of Au-NPs were tabulated in Table 1. Most of the Au-NPs gave spherical shapes and their size was indeed small in the nano-range. This indicate that, plant parts are capable to be a good green reducing agents.

Table 1. Summary of green synthesized Au-NPs using different parts of plants.

Type of plant	Plant part used	Size (nm)	Shape	Surface Plasmon resonance bandwidth (nm)	Application	Reference
Acorus Calamus	Rhizome	10	Spherical	518	Antibacterial and UV blocking for cotton fabric	[49]
Corallocarbus Epigaeus	Rhizome	30	Spherical	545	-	[50]
Glycyrrhiza Uralensis	Root	10-15	Spherical	540	In-vitro	[38]
Cibotium Barometz	Root	5-20	Spherical	548	Antioxidant, antimicrobial agents & drug-delivery agents.	[37]
Euphorbia Fischeriana	Root	20-60	Spherical	540	Inflammatory marker	[51]
Cinnamon	Bark	35	Spherical	535	Fluorescence activity	[39]
Terminalia Mantaly	Bark	22.5 – 43	Spherical	540	In-vitro cytotoxic effect in cancer cells	[40]
Portulaca Oleracea	Leaves	11.34 ± 4.23	Spherical	543	Catalytic activity	[52]
Ricinus Communis	Leaves	200	Spherical	536	Antimicrobial study	[53]
Curcumae Kwangsiensi	Leaves	~8–25	Spherical	539	Anti-cancer	[5]
Digera Muricata	Leaves	33	Spherical	535	Antibacterial activity	[6]
Lawsoniainermis	Leaves	~20	Spherical	540	Catalytic activity	[54]
Solidago Canadensis	Leaves	8-200	Spherical, triangular & hexagonal	530	-	[55]
Mimusops Elengi	Fruit	200-500	Non-spherical	540	Antimicrobial study	[56]
Sambucus Nigra	Fruit	4-80	Spherical	532	Antimicrobial study	[57]
Garcinia Indica	Fruit	11	Spherical & triangular	541	Biological	[48]
Garcinia Cambogia	Fruit	8	Spherical & triangular	541	Biological	[48]
Garcinia Mangostana	Fruit peel	32.96 ± 5.25	Spherical	546	Biomedical	[58]
Lilium Casa Blanca	Flower	5.933 ± 1.158	Spherical	532	Catalytic activity	[59]
Clitoria Ternatea	Flower	13-23	Spherical	550	-	[60]

Platycodon Grandiflorum	Flower	3-80	Spherical	545	Antipathogenic activity	[61]
Catharanthus Roseus	Flower	30-60	Spherical	540	Antibacterial activity	[62]
Garcinia mangostana	Peel	32	Spherical	540–550	-	[63]
Sargassum glaucescens	Marine plant	3.65	Spherical	538	Anticancer Activity	[64]
Hibiscus sabdariffa	leaves	7	Spherical	537	Electrooxidation	[65]
Camellia sinensis	leaves	23	Spherical	529	Computational Modeling	[66]

3. Application in Hybrid Photovoltaic/Thermal System

Constant increase of the demand for electric energy has contributed to wide discovery of the renewable energy that is more environmentally friendly and sustainable if compared to non-renewable energy as it is well-known to contribute to climate change due to an emission of greenhouse gases, in particular carbon dioxide and methane. Most common example of renewable energy is the energy coming from the wind and the sunlight where both resources keep blowing and shining respectively even though their availability are depending on the weather and the time. Nevertheless, solar energy is highly expected to offer greater vital role than the other renewable energy. This is because sunlight is one of the earth's most abundant and freely available energy resources which has leads to wide research attention. An invention of solar collector has been introduced since many years ago in order to capture the solar energy and convert it into useful energy. Despite of many available types of solar collector to harvest the solar energy, it has been reported that an innovation of hybrid photovoltaic/thermal (PV/T) solar collectors can be designed to operate at near 80% in combined efficiency [67]. PV/T system integrates solar photovoltaic and solar thermal collector systems for the co-generation of electrical and thermal power from solar energy [68]. Solar photovoltaic generates electric energy by absorbing solar energy via solar cells. It is an advance technology that has grown leaps and bound particularly over the last two decades but its efficiency still remains around 15-17%. Meanwhile, solar thermal collector refers to a device which collect heat through the sunlight absorption and then transfer it to the heat transfer fluid (HTF) that flowing inside the device [69]. According to Robert A Taylor et al, a well-designed PV/T system will be able to offer a cost-effective system for residential, commercial and industrials usage that needed both electrical and thermal energy [63].

Due to this, many researchers have diverted their attention to the introduction of nanotechnology in order to enhance the overall efficiency of the hybrid PV/T system. In fact, to this day numerous researches have shown that the thermal properties of working fluid in the solar collector system was enhanced by the introduction of nanoparticles. This advanced enhancement was generally done by decorating the conventional working fluid or also known as base fluid such as water, oil and ethylene glycol with functionalized nano-size material (<100nm).

3.1 Utilization of Gold Nanoparticles in Nanofluid-Based Optical Filter for Hybrid Photovoltaic System

Nanofluid-based frequency splitter was a promising method to realize highly efficient full spectrum solar energy utilization. It can generate electricity and achieve high-grade thermal energy simultaneously to fulfil the multi-requirement of heat (or cooling) in commercial/industrial applications, thermochemical processes and even in thermal power generation. Due to the frequency splitter technique, the PVC can work at a relative low temperature to increase the electricity generation efficiency, while the electricity generation efficiency of PVC was not affected or even had a slight increase and the temperature of working was no longer limited by the PVC [63]. Optical filter in hybrid PV/T system had been widely studied to enhance the overall solar energy conversion efficiency in different applications. The theoretical calculation and experimental test indicated that 54.2% more power can be gained when frequency splitter hybrid PV/T system with optimized operation parameters was used [70]. However, the expected overall solar energy conversion performance of the frequency splitter hybrid PV/T system depended strongly on the types of spectral beam splitter, PVC and the requirements of specific applications.

Figure 4 shows the basic schematic of a nanofluid containing Au-NPs in direct absorption solar thermal collector system. The size and shapes of Au-NPs dispersed in the fluid are tunable by the synthesis process and altered accordingly to meet the requirements of the applications.

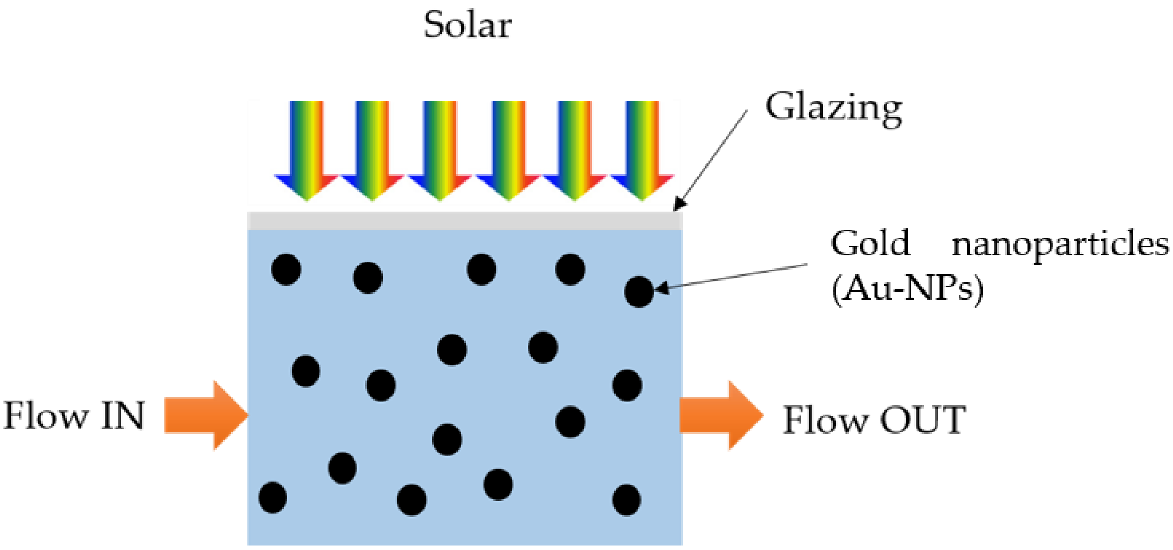

Figure 4. Basic schematic of a nanofluid direct absorption solar thermal collector.

Previous studies by Otanical *et al.* and Robert *et al.* have shown that the efficiency of the solar conversion has surpassing the efficiency of conventional photovoltaic systems based on the modelling studies on the use of nanoparticles as optical filters in hybrid PV/T systems [35-38]. The utilization of Au-NPs suspended in the working fluid of hybrid PV/T systems has gained an attention due to its high surface plasmon resonance (SPR) properties that are highly efficient at absorbing and scattering light. This one particularly notable property of Au-NP has enabled the optical response can be tuned from the ultraviolet through the visible to the near-infrared regions of the electromagnetic spectrum only by changing its size, shape and composition. E. Tunkara et al in their work has combined indium tin oxide and Au-NPs in a silane-based heat transfer fluid that capable of withstanding temperatures up to 340 °C while maintaining spectral transparency at photovoltaic wavelengths. In this research, the indium tin oxide and Au-NPs were synthesized and tailored to achieve particles with solar absorptions outside the photovoltaics spectral window to enhance compatibility with a silane-based heat transfer fluid. Au-NPs were used in this research due to their high localized surface plasmon resonance [71- 73]. M. Du et al in previous work has applied the usage of Au-NPs in their research for working fluid of direct absorption solar thermal collectors (DASC) where Au-NPs with different shapes, sizes, aspects ratios and concentrations were studied numerically. Result shown that the localized surface plasmon resonance of Au-NPs were possible to tune just by adjusting the Au-NPs shape. It also indicated that Au-NPs capable to perform spectral tunability in which will contribute to novel hybrid photovoltaic-thermal (PV/T) system based on nanofluids in the future.

4. Conclusions

Au-NPs is one of the most flourishing among novel metal nanoparticles due to its unprecedented properties that are excellent interaction with visible light and can be used for optimum enhancement of surface plasmon resonance. Other than that, Au-NPs are the most stable metal nanoparticles, and they present fascinating aspects such as their assembly of multiple types involving materials science, the behaviour of the individual particles, size-related electronic, magnetic and optical properties (quantum size effect), and their applications to catalysis and biology. Plant-based materials are useful as the green reducing agent to synthesize Au-NPs due to their high anti-oxidants and bioactive compounds such as phenolic, terpenoid, carotenoids and others. This review paper has included various research that has used all parts in plant as reducing agent such as root/rhizomes, bark, leaves, fruits, fruit peel and flowers and the morphological information was also reviewed in the paper. Next, the usability of Au-NPs in the field of nanofluid-based filter for hybrid photovoltaic-thermal system has been reviewed further and it is concluded that the high surface plasmon resonance in Au-NPs are very useful to the application. The surface plasmon resonance of Au-NPs can be tunable according to their size and shape.

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