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Research paper



A Conceptual Framework on the Green Synthesis of Metal Nanoparticles using Soap Nuts

Praveena Nair Sivasankaran[1]*, Ainon Shakila[2], Tan Sin Jin[3]

[1,2,3,]School of Engineering, KDU University College
**Corresponding author E-mail: praveena.s@kdu.edu.my*

Abstract

Green synthesis of nanoparticles has been an area of interest the past few years due to its promising growth. This conceptual framework paper explores the potential use of Sapindus Mukorossi or better known as soap nuts to be used as the reducing agent in synthesizing metal nanoparticles namely copper, silver and gold respectively. By exploring a greener method to synthesize nanoparticles, many potential application could be explored such as a green filtration technique to provide clean water to billions of people, the increased usage of renewable energy, the reduction of cost for waste management and to explore the possibilities of river reclamation. The usage of metal nanoparticles has been widespread across various fields hence, there is an urge to review its biological and environmental safety during its production. The main methods for nanoparticle production involves chemicals that are potentially harmful to the environment. The usage of plants to transform inorganic metal ions into metal nanoparticles with a capability of heavy metal and toxic accumulation has cultivated interest among researchers. Soap nuts are berries that have saponin as a natural surfactant and this research utilizes the fruits pericarp to synthesize copper, silver and gold nanoparticles. The production of nanoparticles will be studied for its effectiveness and the characteristics of the nanoparticles used for a future project which involves sustainability measures focusing on water filtration systems and river reclamation projects.

Keywords: *Green synthesis; nanoparticles; renewable energy; saponin; soap nuts*

1. Introduction

Nanoparticles are a class of material which possess certain properties which are different from bulk materials. This includes a large surface atom, high surface energy level, unique spatial confinement and reduced area of defects (Laurent et al., 2010). Research studies has found that size is important in influencing the physiochemical properties of an element. Particular characteristics such as the optical properties is heavily dependent on the size of the element. However, nanoparticles synthesis uses harsh and toxic chemicals increasing the concern of toxicity in the environment. This study investigates the synthesis of metal nanoparticles (copper, silver and gold respectively) utilizing *Sapindus Mukorossi* (soap nuts). Studies have shown that plants have the capability to detoxify and accumulate heavy metal [1]. Hence, this "green" approach (using plant extract) has been effectively sought after as a naturally safe technique to synthesize nanoparticles. Paper presents a conceptual framework in outlining the processes involved in synthesizing nanoparticles from these chosen metals. The metal nitrate solutions of copper, silver and gold will be obtained. Each metal nanoparticle chosen has a significant application. Copper nanoparticles are used in antimicrobial agent, medical supplements, electromagnetic shielding (EMI), conductive inks and pastes. Silver nanoparticles is used in multiple applications such as diagnostics, antibacterial, and optical applications. Gold nanoparticles is found to have many potential applications including usage in fuel cells as well as sensory probes, electronic applications, therapeutic agents and photo catalysis [1][2]. Reviews have been conducted to highlights the various types of plant extracts used to create nanoparticles of various shapes and sizes. In this particular study, soap nuts are being used as the main plant extract. Soap nuts contains *Saponin* which are natural surfactants and has been used as a detergent for thousands of years mainly by the natives of Asians and Americans [3]. This study would be the first phase of an ongoing project in usage of nano-metals focusing on sustainability especially in river reclamation and providing clean drinking water using a cost effective method. A bottom up approach is used here to synthesize the particles using soap nuts extract. It is expected that this green synthesis will produce a fine multi shaped particles similar to the synthesis of nanoparticles using the conventional method.

2. Literature Review

The relation between bulk and atomic size material shown by nanoparticles is character-specific. The quantum isolation in semiconductors, resonance of surface plasma and superparamagnetic in magnetic materials are a few of the properties that depends on the size of the particle synthesized [3] [4]. Different properties are shown as the size of a particle approaches the nano-scale. [5]. Nanoparticles gives unpredictable outcomes due to its small size and also due to the adhesion of different type of materials. Different metal nanoparticle records different characteristic. A copper-based material shows bending when the atom are about 50nm. If the atoms are lesser than 50nm, it

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is considered to be hard and cannot be malleable [5]. The change in property may not be favorable. In storing memory, ferroelectric material will change direction according to the room temperature which is a disadvantage. Nanoparticles also tend to sink or float in a solution which creates a concern that needs to be rectified

The synthesized nanoparticles often have unpredictable characteristic such as unknown range of quantum effects. Reducing the size of material affects the quantization effects due to the restriction in movement of electrons. This creates a discrete energy level which is highly dependent on the size of the structure. This knowledge enable us to create an artificial structure with differing properties compared to the bulk material from the respective element. A proper control over structure is necessary to customize the material properties for specific applications. Nanoparticles do not appear as free standing structure as it is normally embedded with a matrix. Siavash stated in his review paper that based on the compilation of previous nanoparticles synthesis application, the nanoparticles produced by plants are more stable compared to the ones produced by other organisms.

Various plants were used to produce nanoparticles. Plants that were studied include henna leaves, mangosteen pericarp, persimmon, peppermint, alfalfa extract and lemon grass [7]. The ability of plants to hyper accumulate metal ions depends on the presence of plant metabolites such as terpenoids, alkaloids, sugars, polyphenols and proteins. These plant metabolites also help in maintaining the stability of the nanoparticles synthesized [9, 20, 22-24]. The concentration of these compounds differ according to the type of plant. This provides an explanation on why the properties of each synthesized nanoparticle is different. The properties are heavily reliant on the reducing or stabilizing agent used (the plant extract solution) [10-11, 24]. The morphology and the size (hexagons, triangles, pentagons, ellipsoids, cubes, spheres, and nano-rods) [11,24].

3. Methodology

3.1. Description of Methodology

There are two ways in synthesizing nano-particles. One is known as the top-down approach and the other one is known as the bottom-up approach. Top down approach involves blasting bigger materials into smaller bits and the bottom up approach uses a salt solution of the metal and a chemical solution (reducing or stabilizing agent) to create the respective nanoparticle. These sedimentation are not water soluble and hence will clump together to form nano-particles. Nanoparticles synthesis involves a bottom-up approach. This paper aims to describe the proposed methodology for the synthesis of 'green' nanoparticles using the bottom-up approach. The first phase of the research involves the synthesis of three different metal nanoparticles namely, gold, silver and copper using the soap nut extract as the reducing agent or stabilizing solution.

3.2 Experimental Variables

In order to synthesize these metal nanoparticles, a range of parameters needs to be controlled such as concentration, heating temperature, RPM or stirring speed and stirring time. Table 1 summarizes the parameters and its respective ranges to be inspected. Briefly, three different reducing or stabilizing agent would be used namely copper nitrate, silver nitrate and gold (III) chloride hydrate would be used. This is pertaining to the type of metal ion that would be used. The important varying factors that should be manipulated would be the concentration of the reducing or stabilizing agent, the heating temperature (this is to control the effect of the size of the nanoparticle produced), the stirring speed after mixing both soap nut extract and the stabilizing agent together and finally the control of the pH. The pH of the stabilizing agent is known to effect the size and morphology of the nanoparticles synthesized. However, there is no concrete research to support these findings. Hence, varying the pH would also be a concern addressed in this research.

Table 1: Experimental variables for the synthesis of metal nanoparticles

Experimental Variables	Soap Nuts Extract	Copper Nitrate	Silver Nitrate	Gold (III) Chloride Hydrate
	Sapindus Mukorossi	$Cu(NO_3)_2$	$AgNO_3$	$HAuCl_4$
Concentration (mol/dm^3)	20-100	6-10	0.5-5	3-8
Heating Temperature (° C)	40-80			
RPM/min	500-3000	400-1200	700-1500	8000-14000
pH (Soap nut extract and salt solution)	2.9-11.2			
Stirring Time/hr	1-24			

3.3. Conceptual Framework

A conceptual framework is used to make conceptual maps and organize ideas. Strong conceptual frameworks captures the project in a way that makes it easy to remember and apply. Fig.1 shows the conceptual framework proposed for this particular study. This paper aims to highlight the proposed methodology of this experiment and to identify and relate the variables in order to design a better experiment. The variables are as shown in Table 1. The design of experiment table can only be created once a few trial and error steps were run throughout the experiment. In the end, the nanoparticles produced should follow the characteristics of the nanoparticles fitting to the application. The later phase of this project involves the photocatalytic properties of the nanoparticles for use in river reclamation or river cleansing system. Hence, the synthesized nanoparticles should possess the characteristics of a filtration device. If the desired properties are not achieved, hence the parameters are modified until the desired characteristic is obtained.

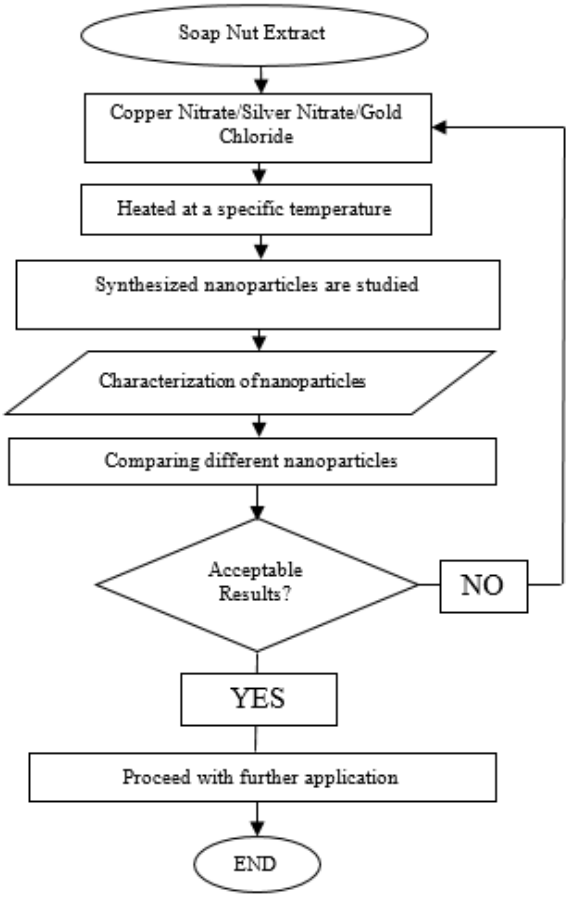


Fig. 1: Conceptual framework on the methodology of synthesizing nanoparticles

3.4. Colloidal method synthesis (in-vitro approach)

Research shows that plants are able to reduce metal ions. Plants have been used to extract precious metals from earth. This extraction will not be economically justified by using conventional methods. Sintering is a process that is used to retrieve the metal after extraction. This sintering of process reveals that the metal extracted were collected in the form of nanoparticles. Studies had been done that shows that alfalfa and mustard leaves accumulate silver nanoparticles with a size of 50nm at a high level (13.6% of its own weight) when silver nitrate is used as a substrate [12].

Certain limitations exist when nanoparticles are synthesized using this method. The active compounds of plants exist in differing concentration depending on the type of the plant. These would affect the metal deposition and the prospect of forming new nanoparticles (nucleation) [23]. The heterogeneity and morphology of the nanoparticles synthesized will be affected as this may limit their use in certain application (that involves precise shape and size). These green synthesis method hence provide a barrier when it is required to meet the market demand. Green synthesis of nanoparticles produces a low yield, with difficulties during the isolation and purification of the nanoparticles from the plant extract. *In vitro* approaches have actively been developed in recent years, believed to rectify these inefficiencies in which plant extracts are used for the bio-reduction of metal ions to form nanoparticles.

In vitro technique gives a flexible option to control the size and morphology of the nanoparticles synthesized. This could be achieved by changing the pH of the medium and the reaction temperature. *In vitro* is much faster than the synthesis of nanoparticles in whole plants, because the reaction is fast without undergoing diffusion of metal ions. In vitro technique has been used for many different kinds of nanoparticles [22,25]

This study requires the usage of ultrapure water of "Type 1" according to the standards of ISO 3696. This ultrapure water uses resin filters and deionization techniques to purify the water. The electrical resistivity of the water will be measured to confirm on the purity. Electrical resistivity shows the ion concentration in water. Higher resistivity shows fewer charge carrying ions. Most ultrapure water is dispensed through a 0.22 μm membrane filter. The usage of pure water is of high importance in this study as such a heavy emphasis is given to the type of water used.

Fifty grams of soap nuts in 500 mL millipore water will be taken in a 250 mL beaker and stirred for overnight on a magnetic stirrer. The mixture will be filtered through the Whatmann No.1 filter study. The filtrate will then be stored under cooling conditions when not used. Five milliliter of the filtrate will be mixed into 1 mM nitrate solutions of the respective metal that needs to be synthesized in 50 mL Millipore water. The solution will be heated to 80°C until a color change appears.

3.5. Characterization of nanoparticles

Characterization of nanoparticles is based on the size, morphology and surface charge, using advanced microscopic techniques such as field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM). Properties such as the size distribution, average particle diameter, charges affecting the physical stability and the in vivo distribution of the nanoparticles will also need to be studied. Properties like surface morphology, size and overall shape are determined by electron microscopy techniques. Features like

physical stability and the polymer dispersion as well as their in vivo performance are affected by the surface charge of the nanoparticles. Therefore it's very important to evaluate the surface charge during characterization of nanoparticles.

3.5.1 Field Emission Scanning Electron Microscopy (FESEM)

A field emission (FE) electron microscope, requires no heat. A "cold" source is employed. The emission of electrons from the surface of a conductor caused by a strong electric field is known as field emission (FE). FE combines with scanning electron microscope (SEM). The SEM is an advanced electron detector. The combination of both FE and SEM produces FESEM (Field emission scanning electron microscope). The electron beam produced by FE is 1000 times smaller than a conventional microscope hence it is necessary to employ these scanning microscopes to study the nanoparticles. FESEM has a high resolution surface imaging which would be beneficial to determine the size and morphology of the nanoparticles.

3.5.2. Transmission Electron Microscope (TEM)

Transmission electron microscope or TEM works on a different concept but it generates an almost similar data to FESEM. TEM sample preparation requires a very thin membrane which is time consuming and complex. A high resolution TEM imaging is critical to study the nano diffraction and atomic resolution. These are critical properties that is required to study the characterization of nanoparticles. In this study, the sample that requires TEM characterization will be deposited onto films. The samples will then be stained using a negative staining material (phosphotungstic). The specimen or sample should be fixed firmly to ensure that it will be able to withstand the vacuum pressure of the instrument. The surface characteristics would be determined when an electron beam is passed through the sample [21].

3.5.3 X Ray Diffraction (XRD)

In order to study the crystallographic structure, chemical composition and physical properties of a nanoparticle (nondestructively) X-ray diffraction techniques are very useful. X ray diffraction is also used to measure the grain size, phase composition and the defective structure. The usage of XRD is proven to be crucial in the study of nanoparticles hence this equipment would be utilized to study the nanoparticles synthesized [17].

3.5.4 Surface Hydrophobicity

There are various techniques that could be used to determine the surface hydrophobicity. This includes adsorption of probes, biphasic partitioning and contact angle measurement. This study uses contact angle measurement to determine the surface hydrophobicity. This characteristic is an important tool to determine the ease of transport of the synthesized nanoparticle and also to measure the level of toxicity [16]. Fig 2 shows an illustration on how the surface hydrophobicity is measured with respect to contact angle.

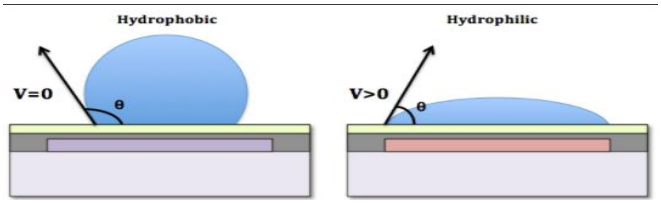


Fig. 2: Hydrophobicity measurement of nanoparticles with respect to contact angle.

3.5.5 Structure Related Photocatalytic Property

The photocatalytic activity of nanoparticles is related by (i) the light absorption coefficient, (ii) the energy of the band gap between valence and conduction band, which should be below energy of the absorbed light, (iii) the electron-hole recombination rate (iv) the absorption of reactants and (v) redox rates on the surface by the electrons and holes [18]. These processes depend on the chemical composition and the nature of the oxide materials. Research shows that by changing the parameters and crystallinity, the rate of photocatalytic activity of a nanoparticle will be enhanced. Fewer bulk defects is ensured by a higher crystallinity rate. The rate of photocatalytic activity of a nanoparticle is ensured by the size, shape and agglomeration (clumping rate). Fig 3 shows a schematic diagram of the intended photocatalytic activity performed by the said nanoparticle

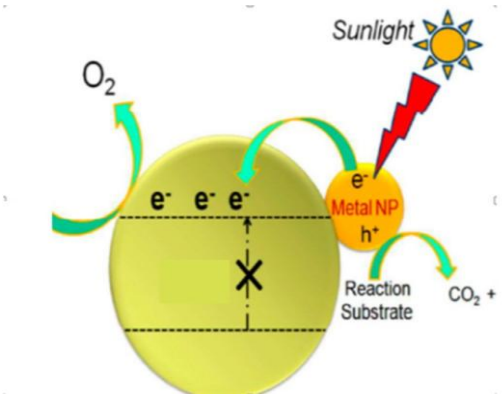


Fig. 3: Concept illustration of a photocatalytic activity of the synthesized nanoparticle

3.5.6. Photocatalytic Tests

This would be the second phase of the study where the photocatalytic test would be included in addition to the traditional characterization method highlighted above. The photocatalytic efficiency of the samples will be evaluated by monitoring the change in optical absorption of a methylene blue (MB) solution, at ~662 nm, (this is the proposed wavelength) during its photocatalytic decomposition process, under UV-light irradiation. Methylene exists as a solid, odorless, dark green powder that yields a blue solution when dissolved in water, at room temperature. It is a common contaminant in wastewater released from industrial (e.g., textile) dyeing processes, which is toxic to human health. All the photocatalysis experiments will be carried out in a photocatalytic reactor. The absorbance of MB will be monitored by a UV-vis spectrophotometer. The following equation will be used to calculate the degradation rate:

$$X = (A_0 - A_t)/A_0 \times 100\% \quad (2)$$

where A_0 is the absorbance of dyes before illumination and At is the absorbance of dyes at time, t.

Conclusion

The paper compiles a detailed conceptual framework intended for the studies of metal nanoparticles which consist of two phases: 1) the green synthesis of metal nanoparticles of soap nuts. And 2) the photocatalytic characterization of the metal nanoparticles synthesized by soap nuts. Based on this framework, it is hoped that by the experimental studies, the metal nanoparticles produced would have the desired photocatalytic property which would later be further exploited in the second phase of this study which is the river reclamation project.

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