POLYPHENOL-MEDIATED GREEN SYNTHESIS OF ZINC OXIDE PARTICLES AND THEIR ANTIBACTERIAL PROPERTIES: A NOVEL SIZE-CONTROLLED APPROACH

NEO ZHI ZING

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Universiti Tun Hussein Onn Malaysia

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To the kid who dreamed to befriend scientists she revered.
Wherever and whoever you will be,
stay curious and never stop learning.

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ABSTRACT

The concept of feasibility in green synthesis of zinc oxide (ZnO) nanoparticles has been discussed thoroughly in many related studies. However, size control using volume of plant extracts undermines potential for process upscaling. This study aimed to improve repeatability and reproducibility of green synthesis of ZnO by controlling total phenolic content of incorporated plant extracts. This study had been conducted by manipulating the molar ratio of zinc nitrate to sodium hydroxide and types of plant extracts. Leaves of *Camellia sinensis*, *Manilkara zapota* and *Elaeis guineensis* had been employed to obtain plant extracts, which were subsequently incorporated at gallic acid equivalent of 100 mgg^{-1}. The phytochemical profile of plant extracts and physical properties of ZnO were determined. In addition, antibacterial activity of dispersed and encapsulated ZnO against *Escherichia coli* and *Staphylococcus aureus* was examined. Consistency in particle sizes of ZnO justified the feasibility of using total phenolic content to achieve size control. The roles of phytochemicals were affected by reaction pH. Under neutral pH, the role of phytochemicals as chelating agent predominated. Under basic condition, complex phytochemicals demonstrated structure-directing effect on ZnO microparticles. The antibacterial strength of ZnO reduced by 16 times with the decrement in particle size. Meanwhile, the incorporation of phytochemicals enhanced antibacterial activity of ZnO by fourfold. Encapsulation retained antibacterial strength of ZnO particles with defined microstructures without enhancement. This study confirmed that particle size and morphology of ZnO could be controlled through manipulation of total phenolic content of plant extracts and the reaction pH of green synthesis.

ABSTRAK

Konsep kebolehlaksanaan dalam proses sintesis hijau terhadap nanopartikel zink oksida (ZnO) telah dibincangkan secara menyeluruh dalam pelbagai kajian yang berkaitan. Walaubagaimanapun, kawalan saiz menggunakan isipadu ekstrak tumbuhan menjejaskan potensi untuk peningkatan skala pemprosesan. Kajian ini bertujuan untuk meningkatkan kebolehulangan dan kebolehan untuk penghasilan semula sintesis hijau ZnO dengan mengawal jumlah kandungan fenolik ekstrak tumbuhan yang digabungkan. Kajian ini dijalankan dengan mengawal nisbah molar zink nitrat kepada natrium hidroksida dan jenis ekstrak tumbuhan. Daun-daun *Camellia sinensis*, *Manilkara zapota* dan *Elaeis guineensis* telah digunakan untuk memperoleh ekstrak tumbuhan yang kemudiannya dicampurkan pada persamaan asid galik sebanyak 100 mgg^{-1}. Profil fitokimia ekstrak tumbuhan dan ciri-ciri fizikal ZnO juga telah ditentukan. Di samping itu, aktiviti antibakteria ZnO sebagai partikel terselerak dan terkapsul terhadap *Escherichia coli* dan *Staphylococcus aureus* telah diperiksa. Ketekalan dalam saiz partikel ZnO menjustifikasikan kebolehlaksanaan penggunaan jumlah kandungan fenolik untuk mencapai kawalan saiz. Peranan fitokimia dipengaruhi oleh pH tindak balas. Di bawah pH neutral, peranan fitokimia sebagai agen pengkelat berdominasi. Di bawah keadaan alkali, fitokimia kompleks menunjukkan kesan pengarahan struktur pada mikropartikel ZnO. Kekuatan antibakteria ZnO berkurang sebanyak 16 kali ganda dengan pengurangan saiz partikel. Sementara itu, penggabungan telah meningkatkan aktiviti antibakteria ZnO sebanyak 4 kali ganda. Penkapsulan mengekalkan kekuatan antibakteria partikel ZnO yang mempunyai struktur mikro yang nyata tanpa sebarang penambahbaikan. Kajian ini mencadangkan bahawa saiz zarah dan morfologi ZnO boleh dikawal melalui manipulasi jumlah kandungan fenolik ekstrak tumbuhan dan juga pH dalam tindak balas sintesis hijau.

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LIST OF SYMBOLS AND ABBREVIATIONS

ANOVA	-	Analysis of variance
BP	-	Baird-Parker
BTLE	-	Crude extract of black tea leaves
CLE	-	Crude extract of *chikoo* leaves
DOM	-	Dissolved organic matter
EDL	-	Electric double layers
EDS	-	Energy-dispersive X-ray spectroscopy
EMB	-	Eosin Methylene Blue
FESEM	-	Field Emission Scanning Electron Microscope
ATR-FTIR	-	Attenuated Total Reflection – Fourier transform infrared
GAE	-	Gallic acid equivalent
HAT	-	Hydrogen atom transfer
HSD	-	Honesty significant difference
IUPAC	-	International Union of Pure and Applied Chemistry
MBC	-	minimum bactericidal concentration
MHA	-	Mueller Hinton Agar
MHB	-	Mueller Hinton Broth
MIC	-	Minimum inhibitory concentration
OPLE	-	Crude extract of oil palm leaves
pKa	-	Acidity value
R	-	Pearson’s correlation coefficient
ROS	-	Reactive oxygen species
SET	-	Transfer reaction of single electron
TPC	-	Total phenolic content
UV-Vis	-	Ultraviolet and visible light

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Nanotechnology is an extensively researched field with an anticipated global market share of approximately 55.0 million dollars by 2022 (Inshakova & Inshakov, 2017. Nanomaterials refer to any material with one or more structures ranging from 1 to 1000 nm, while nanoparticles are materials with all external dimensions within the nanoscale (Jeevanandam *et al.*, 2018). Nanomaterials are classified according to their compositions, which include carbon, organic, inorganic, and composite compounds (Jeevanandam *et al.*, 2018). Metal oxide nanoparticles fall in the category of composite-based nanomaterials.

Metal oxide nanoparticles are synthesized in the laboratory through physical and chemical methods, which include spray pyrolysis, chemical vaporization, sol-gel synthesis, and co-precipiation (Singh *et al.*, 2018; Zikalala *et al.*, 2018). However, the process upscaling through physical and chemical methods suffer from limitations due to the need for sophisticated technology, high-energy consumption, and the use of toxic chemicals (Kharissova *et al.*, 2019). Recent trends in nanosynthesis reveal a growing interest in the use of biological materials to react with metal precursors under regulated condition (Rodríguez-León *et al.*, 2019; Pal *et al.*, 2020). The process simulates wet chemical synthesis without the use of toxic solvents (Singh *et al.*, 2018; Rodríguez-León *et al.*, 2019; Pal *et al.*, 2020).

The terms ‘green synthesis’ and ‘biosynthesis’ are used interchangeably to describe the synthesis of nanoparticles using biological materials derived from bacteria, fungi, algae, and plants (Zikalala *et al.*, 2018). Green synthesis utilizing plant extracts as the bioreductants is a sustainable route since phytochemicals can be extracted from any plant parts (Soni *et al.*, 2021). Green synthesis of metal oxide nanoparticles is cost-effective and environmentally friendly as the required starting materials are metal precursors, plant extracts, and water (Singh *et al.*, 2018; Zikalala *et al.*, 2018). Phytochemicals also function as capping agents to control the morphology and particle size of nanoparticles in addition to being the reducing and chelating agents (Singh *et al.*, 2018; Zikalala *et al.*, 2018).

Zinc oxide (ZnO) nanoparticles have garnered attention for a wide range of applications due to their unique physical and chemical attributes. Zinc oxide nanoparticles had been reported as photocatalytic adsorbent for water treatment (Ong, Ng & Mohammad, 2018; Isik *et al.*, 2019), gas sensors (Han *et al.*, 2010; Rai & Yu, 2012), solar cells (Saeidi, Abrari & Ahmadi, 2019; Trindade *et al.*, 2020), and active ingredient in cosmetics (Kuo *et al.*, 2010; Lu *et al.*, 2015). Meanwhile, the biocidal effect of ZnO nanoparticles against pathogenic microorganisms had captured attention for their potential commercialization as preservatives and biocidal products (Clausen *at al.*, 2011; Pasquet *et al.*, 2014; Król *et al.*, 2017).

The versatility of ZnO nanoparticles has prompted the development of their green synthesis pathway with the incorporation of different plant extracts. Despite extensive efforts to justify the pathway's feasibility, the processing conditions are not universal. The incorporation of plant extracts is expressed in weight, volume or percentage without quantitative and qualitative information of the phytochemicals present in the reaction. Xu *et al.* (2021) highlighted plant extract concentration as one of the the major manipulating factors in green synthesis of ZnO nanoparticles in addition to plant species, precursor concentration, reaction time, pH value, and calcination condition. Even though a trend was observed where the size of nanoparticles reduced with the increment in concentration of incorporated plant extract, the process was not replicable because the unit used to express the incorporation of plant extract was empirical. Uncertainties in phytochemical content are contributed by genomic composition, developmental stage, cultivation condition of plants, and sensitivity of phytochemicals to time and temperature control during extraction (Dhami & Mishra, 2015; Altemimi *et al.*, 2017).

Owing to the uncertainties, a rapid and effective quality control plan is desirable to improve the repeatability and reproducibility for green synthesis of ZnO nanoparticles. Instead of incorporating the plant extracts on an empirical basis, it is ideal to exert control on biological active compounds present in the extracts.

Polyphenols, constituted of flavonoids and non-flavonoids compounds, are the most prevalent phytochemicals in plant kingdom (Câmara *et al.*, 2020). Polyphenolic compounds are regarded as marker group for quality evaluation of medicinal plants due to their substantial influence in biological activity of extracts (Belščak-Cvitanović *et al.*, 2017). In fact, study has been carried out to determine the role of isolated phenolic acids in the green synthesis of metal nanoparticles (Amini & Akbari, 2019).

Meanwhile, the application of ZnO nanoparticles as antibacterial agent is restricted to colloidal stability of the nanoparticles and the chemistry of administered condition (Peng *et al.*, 2017). When dispersed into targeted site, zinc oxide nanoparticles are prone to forming agglomerates (Tso *et al.*, 2010; Keller *et al.*, 2010; Peng *et al.*, 2015). Encapsulation of nanoparticles in supporting medium improves their dispersibility and stability (Trujillo-Reyes, Peralta-Videa & Gardea Torresdey, 2014). The encapsulation of ZnO nanoparticles in alginate nanocomposites has shown its applicability as disinfectant (Zhang *et al.*, 2015; Motshekga, Ray & Maity, 2018; Baek, Joo & Toborek, 2019). However, it is important to highlight that the attack mechanisms of ZnO nanoparticles against microorganisms are determined by their morphology and particle size. The attack mechanisms of ZnO nanoparticles include generation of reactive oxygen species (ROS), bacterial cell internalization and destruction, and release of Zinc (II) ions (Zn^{2+}) (Dimapilis *et al.*, 2018). Previous studies demonstrated the antibacterial properties of ZnO nanocomposite without taking into account the differences in antibacterial strength contributed by morphology and particle size of the encapsulated nanoparticles. Thus, more research is required to provide information on feasibility of the concept when the variability in morphologies and particle sizes of ZnO nanoparticles is a concern.

As an emerging multidisciplinary field of material chemistry, biotechnology and nanotechnology, the application of different plant extracts in green synthesis of ZnO nanoparticles has been widely explored. This study is a fundamental research conducted with the goal of improving the repeatability and reproducibility of green synthesis for ZnO size control. This study was also intended to elucidate the reaction mechanism of green synthesis of ZnO nanoparticles. In addition, the current work was envisioned to contribute to the future design of deployment techniques for ZnO nanoparticles as biocidal products.

1.2 Problem statement

The feasibility for the green synthesis of ZnO nanoparticles has been proven through extensive studies with the application of different plant extracts. Previous research focus on manipulating of reaction duration, temperature, pH, concentration of precursors and plant species for desirable process outcome. Generally, plant extracts are cited as reducing agents in green synthesis of ZnO nanoparticles, with their incorporation regulated by percentage in reaction mixtures (Xu *et al.*, 2021). Despite being a major player in green synthesis, plant extracts inclusion was manipulated merely by the volume of aqueous extract added, without information on the quantitative and qualitative phytochemical profile. The variability of phytochemical composition in extracts reduces the repeatability and reproducibility of green synthesis. Present study was carried out to address the issue.

Zinc oxide nanoparticles are made up of ZnO particles with various particle sizes and morphologies. The morphology and size of ZnO nanoparticles determine their attack mechanisms against microorganisms. The ideal deployment practice of ZnO nanoparticles as effective biocidal agent shall take their physical properties into consideration. Encapsulation of ZnO nanoparticles in polymeric network is trending in efforts to resolve problems associated with agglomeration and settling of nanoparticles following administration to liquid medium. Previous studies focused mainly on investigating the difference in antibacterial properties between individual nanoparticles and their encapsulated counterparts. It is prudent to investigate the universality of encapsulation for ZnO of different morphologies in order to enhance their antibacterial strength. To address the issue, ZnO nanoparticles with distinct morphologies and particle size were examined for their antibacterial strength as dispersed and encapsulated particles under controlled conditions.

1.3 Research objectives

The aim of the study was to improve repeatability and reproducibility of ZnO green synthesis. In addition, proposal of reaction mechanism and the roles of phytochemicals in green synthesis of ZnO were anticipated. The antibacterial activities of ZnO against *Escherichia coli* and *Staphylococcus aureus* were also investigated, with respect to morphologies, particle sizes and deployment methods.

The objectives of the study are as follows:

I. To synthesize ZnO nanoparticles by incorporating different plant extracts at controlled total phenolic content.

II. To determine the effects of reaction condition and phytochemical composition on morphology and particle size of ZnO.

III. To examine the antibacterial activity of ZnO samples against *E. coli* and *S. aureus* as dispersed particles and encapsulated particles.

1.4 Scopes and limitations of study

The following are the scopes of study adopted to fulfil the objectives:

I. The selection of plant leaves for this study was derived from three categories; food material for *Camellia sinensis* (black tea leaves), traditional herbal medicinal material for leaves of *Manilkara zapota* (*chikoo* leaves) and waste material for the leaves of *Elaies guineensis* (oil palm leaves). Plant materials were decocted through aqueous extraction to eliminate the use of solvent. Prior to the synthesis of ZnO, total phenolic content of crude extracts were examined using Folin-Ciocalteu assay to obtain data on concentration of gallic acid equivalent (GAE). Plant extracts were incorporated at a concentration of 100 mg GAE g^{-1}. The reaction mixtures were prepared at different molarity combinations of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$] and sodium hydroxide (NaOH).

II. The morphology and particle size of ZnO were examined under Field Emission Scanning Electron Microscopy (FESEM). Due to large numbers of ZnO samples synthesized, representative samples from replicated procedure were prepared for observation under FESEM. The consistency of particle sizes in ZnO samples was considered a measure of repeatability of process. Meanwhile, the phytochemical composition of plant extracts were determined with Attenuated Total Reflection - Fourier Transfrom Infrared (ATR-FTIR) spectroscopy and standard methods of phytochemical qualitative analysis. The information on reaction mixture, qualitative phytochemical data and physical properties of ZnO were integrated to determine their interrelated effects and elucidate the reaction mechanisms.

III. The minimum inhibitory concentration (MIC) of ZnO against *E. coli* and *S. aureus* was determined using Resazurin Cell Viability Test. The bacterial suspension was prepared in 0.9 % saline solution instead of broth medium to eliminate the interference of organic compounds from the culture medium. In addition, only ZnO with defined microstructures and ZnO nanoparticles of the smallest sizes within the group of incorporated crude plant extract were selected for the examination of antibacterial activity as encapsulated particles. The ZnO samples were encapsulated in alginate hydrogel beads. The antibacterial activity of encapsulated particles were determined using a modified Kirby-Bauer method.

IV. Statistical analysis was performed using IBM SPSS Statistics 22.0 to compare the means of independent groups and determine the correlation between groups of variables.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanomaterials and nanoparticles

Nanomaterials are defined as materials with at least one dimension smaller than 1 μm (Buzea, Blandino & Robbie, 2007). While they share the same definition, nanoparticles are characterized by the potential to be in smaller scales, such as atomic and molecular scales (approximately 0.2 nm) (Buzea, Blandino & Robbie, 2007). Meanwhile, a bulk material could be interpreted as particles without definite geometries (Walter, 2013). A nanoscale material exhibits distinct characteristics from its bulk counterpart because of its higher aspect ratio (Aljawfi *et al.*, 2020). Surface and quantum effects are two factors that cause behavioral differences between nanomaterials and bulk materials (Buzea, Blandino & Robbie, 2007; Aljawfi *et al.*, 2020). The nanoparticles exhibited nano effects due to their outstanding optical, thermal, magnetic, mechanical, and electrical properties.

Nanoparticles can be classified into primary particles, agglomerates, and aggregates based on their morphologies. Primary particles can be regarded as nanoparticles with well-defined geometrical shapes. Because of their high surface energy, the primary particles are prone to assembling into agglomerates. The surface area of agglomerates is not much different from that of primary particles (Walter, 2018). The International Union of Pure and Applied Chemistry (IUPAC) defines agglomerates as dispersed particles held together by weak physical interactions. In the wet chemical synthesis method, the formation of agglomerates results in precipitation of nanoparticles when they exceed their colloidal sizes (Sokolov *et al.*, 2015). The formation of agglomerates is reversible under specific temperature, pressure, and solution pH (Sokolov *et al.*, 2015). Meanwhile, aggregates form as the primary particles crystallize. Aggregates are interpreted as strongly bonded colloidal particles produced by irreversible clustering (Sokolov *et al.*, 2015). Crystallization of primary particles occurs during the sintering process, resulting in the formation of aggregates. These aggregates have a much lower specific surface area than their primary particles. Figure 2.1 depicts the difference between primary particles, agglomerates and aggregates.

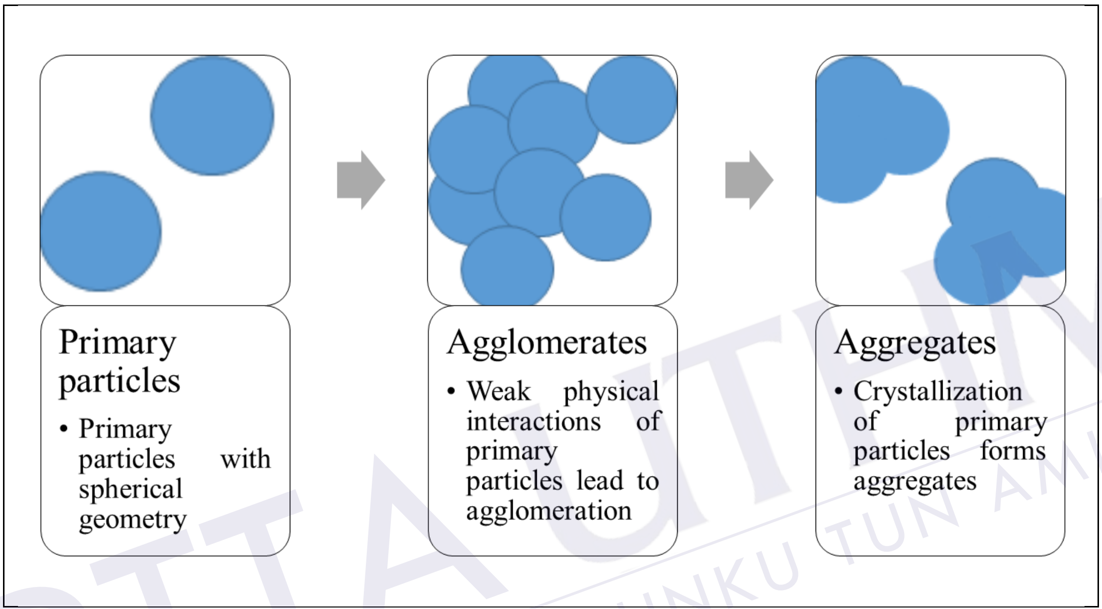

Figure 2.1: Primary particles and agglomerates exhibit similar surface area to volume ratio; however, the aggregates have a much smaller specific surface area compared to the others.

2.2 Nucleation and growth of nanoparticles

LaMer's mechanism is used to conceptualize the synthesis of nanoparticles. The mechanism is characterized in terms of two sequential stages: nucleation and growth (Thanh, Maclean & Mahiddine, 2014; Polte, 2015). The prerequisites for condensation, which are the zero-charge precursors, are formed through redox reaction. The solution will become saturated with the monomers as nucleation continues. When the nucleation threshold is reached, nanoparticles begin to grow. Nuclei can grow isotropically when the rate of growth is slower than the rate of nucleation or anisotropically when the conditions are reversed (Zikalala *et al.*, 2018). These particles will continue to grow unless they are stabilized by counteractive repulsive force (Polte, 2015). The factors governing growth of nanoparticles are surface energy and solubility of nanoparticles.

2.3 Nanosynthesis

The process of generating nanoparticles is known as nanosynthesis. There are two approaches of nanosynthesis: top-down and bottom-up. The top down approach to nanosynthesis is to reduce the size of the starting material to the nanoscale using mechanical and chemical methods (Goyal, 2017). Meanwhile, the bottom-up technique involves the building of nanoparticles atom-by-atom, molecule-by-molecule or, cluster-by-cluster (Goyal, 2017). There are three primary methods for producing nanoparticles: chemical, physical and biological syntheses. Because of growing environmental concerns, biological synthesis, which employs waste materials, microbes, and plants as reducing media, is being intensively investigated (Zikalala *et al.*, 2018). Biological synthesis is also referred to as green synthesis. The core concepts of green synthesis include waste minimization, pollution reduction, the use of safer solvent, and the incorporation of renewable feedstock (Singh *et al.*, 2018). Overall, green synthesis is regarded as a reliable and sustainable synthesis pathway (Singh *et al.*, 2018).

2.3.1 Green synthesis of nanoparticles

Phytosynthesis is the synthesis of nanoparticles with the incorporation of plant extract. The term "phyto" is derived from the Greek word "phutón", which means "plant". Phytosynthesis is a burgeoning sub-discipline of nanosynthesis. Green synthesis is a more popular term to describe the process. Metal ion transformation into nanoparticles is a natural process in plant metabolism (Zikalala *et al.*, 2018). In the process of phytomining, uptake and assimilation of metal ions will ultimately lead to conversion of ions into nanoparticles with the utilization of plant biomaterials as capping agents (Zikalala *et al.*, 2018).

The prerequisites for green synthesis of metal nanoparticles are reducing or chelating agents from plants and a precursor of the desired metal. Metal complexes are formed as a result of interaction between the reducing or chelating agents and the metal precursor. Reducing agents are chemical compounds that reduce another chemical compound by donating electrons while chelating agent are ligands that may form two or more coordinating covalent bonds with a metal ion. The roles of plant extracts vary as the reaction conditions change. Moreover, phytochemicals could function as capping agents, forming electrostatic interaction with metal complexes to stabilize the particles.

According to previous studies, polysaccharides, reducing sugars, amino acids, organic acids, vitamins, and phytochemicals act as reducing, chelating, and capping agents in phytosynthesis (Duan, Wang & Li, 2014; Singh *et al.*, 2018; Sharmila, Thirumarimurugan & Muthukumaran, 2019). The ability of phytochemicals to facilitate the formation of metallic and metal oxide nanoparticles is governed by the reducing properties of their functional groups. Previous studies has linked metal bioreduction to the presence of hydroxyl (-OH) and carbonyl (C=O) in phytochemicals such as phenols, alkaloids, flavones, and anthracenes (Singh et al., 2018; Ishak, Kamarudin & Timmiati, 2019; El Shafey, 2020). Additionally, El Shafey (2020) also reviewed that the oxygen produced from degradation of phytochemicals assisted the reduction of metal compounds.

Previous studies highlighted the feasibility of using the leaf extract of *Camellia sinensis*, *Manilkara zapota* and *Elaies guineensis* in green synthesis of metal and metal oxide nanoparticles (Ramli *et al.*, 2015; Asghar *et al.*, 2018; Shaniba *et al.*, 2019; Satheesha *et al.*, 2020; Kiriyanthan *et al*, 2020). The properties of tea products vary depending on the processing conditions of *Camellia sinensis*. The fermentation of *Camellia sinensis* leaves results in the production of black tea leaves (Chan, Lim & Chew, 2007). In Malaysia, black tea is a common commodity. Zhao *et al.* (2019) reported the prevalence of polyphenolic compounds in black tea, particularly catechins and theaflavins. Meanwhile, *Manilkara zapota*, commonly known as *chikoo* or *ciku*, is a lowland rainforest species commonly farmed in Malaysia for its wholesome fruits (Tamsir *et al.*, 2020). Decoction of *chikoo* leaves has been deployed as traditional medicine to treat inflammatory diseases (Islam *et al.*, 2013). Tamsir *et al.* (2020) reported high total phenolic content in *chikoo* leaf extract, with a high concentration of m-coumaric acid and quinic acid. The use of leaf extract of *Elaies guineensis*, also known as oil palm, in green synthesis of metal nanoparticles has been introduced due to the presence of antioxidative polyphenols with hydroxyl and carboxyl groups (Ramli et al., 2015). Oil palm leaf extracts were reported to contain alkaloids and terpenoids in addition to phenolic compounds (Ng, Abdullah & Chong, 2013). Figure 2.2 depicts the chemical structures of common polyphenolic compounds found in plant extracts.

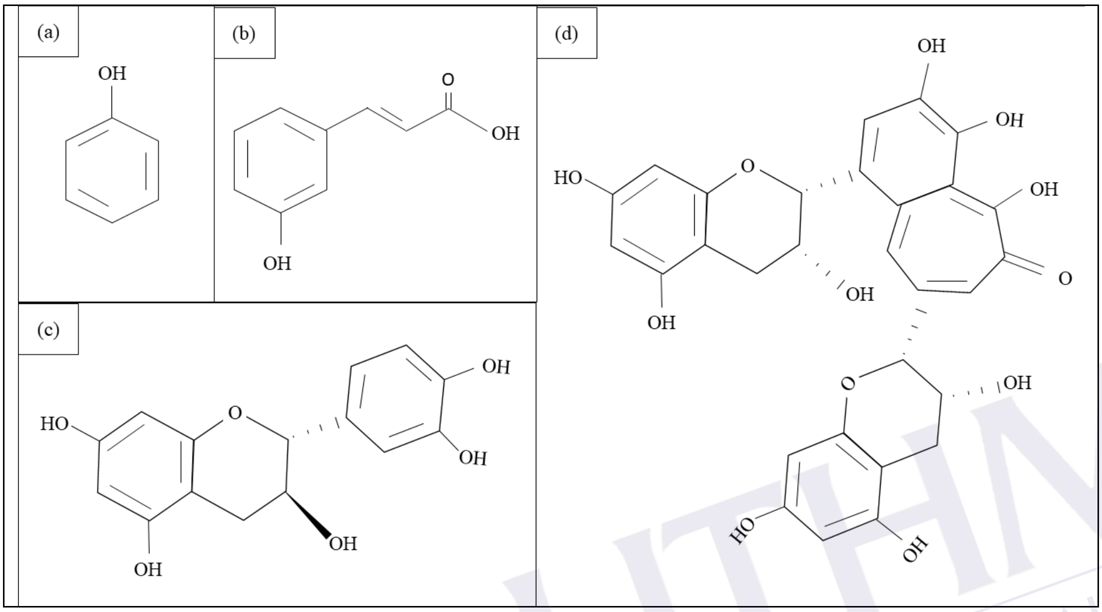

Figure 2.2: Phenolic compounds with hydroxyl groups, for instances (a) carbolic acid, (b) m-coumaric acid, (c) catechin, and (d) theaflavin, are postulated to have contributed to the reducing properties of plant extracts.

2.3.2 Controlling parameters of green synthesis

The size and morphology of nanoparticles are manipulated by an interplay of various process parameters, such as volume of plant extracts, reaction pH, reaction time and temperature, the nature and concentration of precursor and reducing agent, and the synthesis protocol (Ajdari *et al.*, 2017; Ismail *et al.*, 2018; Rodríguez-León *et al.*, 2019). It is important to note that previous studies have focused on volume rather than concentration and quality of plant extracts.

The effect of pH on size and morphology of nanoparticles is proven significant (Patra & Baek, 2014). The pH value of reaction mixture manipulates the oxidation state and reducing power of the reducing agents (Kumari *et al.*, 2016; Ismail *et al.*, 2018). In addition to initiating nucleation, reaction pH affects the solubility of primary particles. The concentration of primary particles is important for controlling of particle size during nanosynthesis (Gogotsi, 2006). Ostwald ripening occurs when the

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