SYNTHESIS OF SILICA AND CARBON NANOPARTICLES FROM RICE HUSKS FOR LATENT FINGERMARKS APPLICATION

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By

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LIST OF ABBREVIATIONS

APVC	-	Acrylic polyvinyl chloride
BET	-	Brunauer- Emmett-Teller
BJH	-	Barrett–Joyner–Halenda
BP	-	Black powder
CNP	-	Carbon nanoparticle
DFO	-	1,8-Diazafluoren-9-one
DNA	-	Deoxyribonucleic acid
EDS	-	Energy Dispersive X-Ray Spectrophotometer
FESEM	-	Field Emission Scanning Electron Microscope
FTIR	-	Fourier Transform Infrared Spectrophotometer
GNP	-	Gold nanoparticle
HCl	-	Hydrochloric acid
HRTEM	-	High Resolution Transmission Electron Microscope
ICPMS	-	Inductively Coupled Plasma Mass Spectrophotometer
IR	-	Infrared
KBr	-	Potassium bromide
MMD	-	Multimetal Deposition
NaOH	-	Sodium hydroxide

NPR	-	Nanoparticle Reagent
QD	-	Quantum dots
RH	-	Rice husk
RHA	-	Rice husk ash
SEM	-	Scanning Electron Microscopy
SiNP	-	Silica nanoparticle
$SiNP_{sp}$	-	Silica nanoparticle$_{\text{solvent precipitation}}$
$SiNP_{me}$	-	Silica nanoparticle$_{\text{microemulsion}}$
SMD	-	Single Metal Deposition
SPR	-	Small Particle Reagent
SS	-	Sodium silicate
SS_{rh}	-	Sodium silicate$_{\text{rice husk}}$
TEM	-	Transmission electron microscopy
TEOS	-	Tetraethyl orthosilicate
UV	-	Ultraviolet
UV-Vis	-	Ultraviolet-Visible
WP	-	White powder
XPS	-	X-Ray Photoelectron Spectrophotometer
XRD	-	X-Ray Diffraction analysis

SINTESIS NANOPARTIKEL SILIKA DAN KARBON DARIPADA SEKAM PADI UNTUK APLIKASI CAP JARI PENDAM

ABSTRAK

Mutakhir ini, penyelidikan yang melibatkan teknik penimbulan cap jari pendam (CJP) telah mengambil pelbagai laluan dalam usaha para penyelidik meneroka kaedah alternatif untuk meningkatkan keberkesanan serbuk dan reagen yang sedia ada. Pelbagai kajian tentang kesan penggunaan sebatian nano untuk meningkatkan sensitiviti dan selektiviti serbuk cap jari yang boleh menimbulkan CJP dengan kejelasan dan kontrast yang tinggi aktif dijalankan. Namun, aplikasi nanoteknologi dalam penyiasatan rutin adalah terhad disebabkan oleh kekangan kos, syarat aplikasi yang ketat dan juga sifat toksik nanopartikel sintetik. Dalam kajian ini, kaedah sintesis yang baru telah dibangunkan untuk sintesis nanopartikel silika (NS) dan karbon dengan menggunakan sumber mesra alam, sekam padi (SP). Proses pencernaan asid telah dijalankan untuk menyingkirkan sisa kotoran logam dari SP. Sisa penapisan telah diabukan untuk mengestrak silika, manakala baki cecair pula dipanaskan untuk membentuk nanopartikel karbon (NK), teknik sintesis NK yang baru. Natrium silikat telah dijana dengan melarutkan abu SP tulen yang diperolehi dari proses penulenan berperingkat, dalam solusi alkali. Pemendakan NS yang berbentuk sfera, tidak beraglomerasi dan mempunyai purata saiz partikel 270 nm dengan menggunakan asid asetik dan aseton juga diterajui dalam kajian ini. Komposisi kimia dan ciri amorfos silika telah ditentukan dengan menggunakan teknik analisa spektroskopi. Pengeringan beku menghasilkan serbuk NS yang mempunyai isipadu liang mesoporos (0.167 cm^3/g), purata saiz liang 4.2 nm (0.9 hingga 57.90 nm distribusi saiz liang) dan jumlah luas permukaan yang tinggi (162.00 m^2/g (Brunauer-Emmett Teller), (BET) dan

238.60 m^2/g Barrett-Joyner-Halenda (BJH)). Proses penuaan sisa cecair dari pencernaan asid SP pula telah menghasilkan NK yang mempamerkan ciri-ciri partikel yang berbentuk sfera, berpermukaan kasar dengan tahap aglomerasi yang lebih tinggi berbanding NS. Distribusi saiz partikel NK adalah dalam linkugan 100 hingga 500 nm dengan saiz partikel purata 300 nm. Ikatan molekul dan komposisi kimia NK telah disahkan dengan menggunakan teknik-teknik spektroskopi. Serbuk NK mempunyai isipadu liang mikroporos (0.009 cm^3/g), saiz liang purata 61.75 nm (0.89 hingga 81.90 nm distribusi saiz liang) dan jumlah luas permukaan yang rendah (0.558 m^2/g BET dan 4.816 m^2/g BJH). NS yang dibentuk telah digunakan dalam tiga produk berbeza; serbuk nanopartikel putih, reagen nanopartikel serta serbuk nanopartikel pelbagai warna, manakala NK digunakan sebagai serbuk nanopartikel hitam. Pendekatan metodologikal telah diambil untuk membandingkan keberkesanan serbuk nanopartikel dengan serbuk cap jari komersial untuk penimbulan CJP pada peringkat penuaan yang berbeza. Sistem skor standard telah digunakan untuk menilai keputusan dan analisa statistik digunakan untuk mendapatkan kesimpulan data. Dapatan kajian menunjukkan bahawa keberkesanan serbuk nanopartikel adalah setanding dan adakalanya lebih baik dari serbuk komersial pada permukaan yang tertentu. Sintesis nanopartikel ini menggunakan bahan mentah yang murah tidak memerlukan alatan khas, penambahan resin, molekul pelekat atau proses pasifasi permukaan. Selain itu, penggunaan SP dapat meningkatkan sumber kewangan para petani dan juga mengabungkan kaedah nanoteknologi yang mesra alam dalam siasatan kriminal rutin. Secara konklusi, produk-produk murah yang telah dicadangkan mempamerkan kualiti lebih unggul dan superior berbanding dengan produk dalam pasaran kini.

SYNTHESIS OF SILICA AND CARBON NANOPARTICLES FROM RICE HUSKS FOR LATENT FINGERMARKS APPLICATION

ABSTRACT

Research into latent fingermark developing techniques has taken many paths over the years as researchers and practitioners explore numerous methods to enhance existing powders and reagents. Currently, copious research is being dedicated to investigating the transformational improvements that could be provided by nanosized compounds to expand the sensitivity and selectivity of fingermark dusting powders to develop fingermarks with high clarity and better contrast. Nonetheless, such a technique has inherent drawbacks of limited field applicability, cost and energy intensive, incurs health hazard to the users in the long run as well as prepared using synthetic precursors. In this research novel synthesis techniques of silica nanoparticle (SiNP) and carbon nanoparticle (CNP) from a sustainable eco-friendly source, rice husk (RH) was developed. Acid digestion process was conducted to remove trace metal impurities from RH. The filtrand was ashed to extract silica, while the filtrate was aged to form CNP, a novel CNP synthesis technique pioneered in this research. Sodium silicate was formed by dissolving highly pure rice husk ash, obtained from the stepwise purification of RH, in alkali solution. Precipitation of SiNP using acetic acid and acetone is introduced in this research to form minimally agglomerated, well dispersed spherical SiNP with a mean particle size of 270 nm, verified using imaging techniques. Silica chemical composition and amorphous nature were confirmed by using spectroscopic analysis. Freeze-drying produced mesoporous pore volume (0.167 cm^3/g) silica powders with a 4.2 nm average pore size (0.9 to 57.9 nm pore size

distribution) and very high specific surface (162.00 m^2/g (Brunauer-Emmett Teller, (BET) and 238.60 m^2/g Barrett-Joyner-Halenda (BJH)). Ageing of the filtrate from acid digestion produced amorphous CNP that exhibited non-smooth, slightly irregular spherical particles with a higher degree of agglomeration in comparison to SiNP. Particle size distribution fell in the range of 100 to 500 nm with mean particle size of 300 nm. Molecular bonding and chemical composition of the CNP was confirmed using spectroscopic techniques. CNP powder possessed microporous pore volume (0.009 cm^3/g) with a 61.75 nm average pore size (0.89 to 81.90 nm pore size distribution) and low surface area value (0.558 m^2/g BET and 4.816 m^2/g BJH). Spherical SiNP obtained was formulated into three derivative products namely white nanoparticle powder, nanoparticle reagent (NPR) and multicoloured nanoparticle powder, while the CNP powder was used as the black nanoparticle powder. A methodological approach was conducted to compare the efficiency of the nanoparticle products against commercial products by developing fresh and aged fingermarks of various stages. Standard scoring system was applied to evaluate the results and statistical analysis was employed to summarise the data. Findings revealed that the nanoparticle powders and reagent performed on par with the existing commercial powders while exhibiting higher selectivity. Nanoparticle synthesis from low cost precursor in this research did not require special equipment, addition of resins/adhesives or surface passivation. Additionally, utilisation of RH may boost farmer's income and incorporate non-toxic green nanotechnology into routine investigative procedures. In conclusion, the low cost products developed exhibited promising quality and superiority to the existing products in the market.

CHAPTER 1

INTRODUCTION

1.1 Research background

Fingermarks are the most affirmative biometric evidence. There are continuous efforts to broaden new techniques and improving current techniques of fingermark development with enhanced sensitivity (Becue *et al.*, 2007). The improved technique is aimed to produce fingermarks with better clarity and resolution at various stages of ageing regardless of surface porosity. Increasingly more innovative strategies are advanced targeting precise components of fingermark residue simultaneously improving the sensitivity of the technique and enhancing contrast (Drapel *et al.*, 2009). In this line, luminescent fingermark visualisation offers remarkable advantages on a wider variety of light, dark and patterned surfaces providing enhanced contrast (Sodhi and Kaur, 2008).

Nanotechnology is a fascinating branch of science. Physicochemical properties of nanomaterial tuneable by size modulation offer uncountable opportunities for surprising discoveries (Heiligtag and Niederberger, 2013). Incorporation of nanotechnology in diverse fields has brought fundamental improvement including the sector of forensic science specifically in latent fingermark development techniques (Zaman *et al.*, 2014). Nanoparticles can be exploited in designing new fingermark dusting powders and reagents with expanded selectivity and sensitivity (Dilag *et al.*, 2011).

Nanoparticles are small in size, versatile and their surface properties may be tuned according to the needs which lead to the precise targeting of a specific component of

fingermark residue apart from the underlying substrate (Moret *et al.*, 2014). However, the commercialisation of those new techniques is often limited due to employment conditions, the limited mobility of the substrate bearing fingermark or the increased health hazard to the consumer (Becue *et al.*, 2011). An ideal and improved product should no longer offer only enhanced selectivity and sensitivity but also may be employed for regular use without or with minimal health threat to consumers (Becue *et al.*, 2007).

1.2 Fingermarks and forensic investigations

The use of ridge impressions has been recorded as early as 221 B.C in a Chinese document and since then the evidentiary evolution of fingermarks has only solidified its undisputed value (Voss-De Haan, 2006). Fingermarks are surely one of the most crucial and incriminating proof in the course of a criminal investigation. Lower processing fee and concrete fundamental science behind dactylography make fingermark evidence very valuable to crime scene professionals (Barnes, 2011). Fingermark does not best serve to link the crime scene to a suspect alone but may also be used as a mean of victim identification and exoneration of the innocent.

The first case known to man to have secured a conviction primarily based on fingerprint evidence took place in Bengal in 1898 (Sodhi and Kaur, 2005). Alphonse Bertillon solved a murder in France, Paris via matching a fingermark found at a crime scene with his anthropometric cards (SIRCHIE, 2011). This incident instigated the cascade of cases using fingerprints as a treasured tool for identification in forensic science. Studies have been carried out to continue improving method of detection, recovery and identification of fingermark.

Most of the time, fingermarks require development to permit the visualisation. Abundant physical and chemical techniques are currently dedicated for this purpose. All of the techniques have inherent limitations in their application or efficiency. Factors such as nature of substrate bearing the fingermark, conditions of fingermark recovery, and the composition of the fingermark residue and age of the recovered fingermark play a major role in influencing the capability of a technique.

1.3 Problem statement

The detection, comparison and identification of fingermarks remain the best means of providing links between the trifecta of crime; the victim, crime scene and the perpetrator. Significant ongoing research is being directed to improve the sensitivity of the existing latent fingermark development methods owing to the fact that current techniques may not be effective on weak fingermarks or reveal sufficient ridge details for identification (Lennard, 2014). In spite of the paramount value of fingermarks as an identification tool, the recovery rate of latent fingermarks found in crime scenes is not at a satiable level. Loss of fingermarks may be attributed to the destructive environment such as human act, arson, explosion, rain and natural conditions of ageing (Dhall and Kapoor, 2016). Fingermark developing products that are currently in commercial use poses several disadvantages including high cost, increased health hazard, non-specific interaction with ridge residue and background, requires the use of one brush for each powder as well as environmental contamination (Lee and Gaensslen, 2012; Daluz, 2015).

The effectiveness of fingermark development heavily relies on the size and shape of the fingerprint powder particles. Optimal fingerprint developing products would have the following attributes; small, rounded and well-dispersed particles, which has a high

affinity for the fingermark residue but exhibits minimal interaction with the substrate bearing the fingermark (Sodhi and Kaur, 2001). Smaller and rounded particles have better adherence and create a uniform layer on the ridge than large coarse particles. Other added advantage of an optimal product would include increased stability, cost-effective, field-friendly, easy manufacturing from a sustainable source and poses a minimal health hazard for the users (Fernandes *et al.*, 2015). However, most commercial formulation still utilises fine nanostructured particles in the range of one to ten micrometres (Sodhi and Kaur, 2001). These particle does not have any specific affinity for fingermark residue and this characteristic leads to non-specific interaction between fingermark residue and the particles (Becue *et al.*, 2009).

Besides, commercial fingerprint dusting powders may cause great health hazard in the long term. Although a substantial amount of fingerprint powder may be inhaled by the crime scene professionals and police personnel during crime scene analysis, secondary exposure from contaminated clothing was deemed to be more harmful. Health hazard from the long-term exposure to fingerprint dusting powder is caused by the presence of trace metals that lead to heavy metal toxicity (Netten *et al.*, 1990; Maynard, 2011). Exposure to fingerprint dusting powders can cause skin rashes and visual impairment in the long run (Souter *et al.*, 1992).

Although nanoparticle-based techniques and powders have been extensively researched in the past and continuing efforts are being undertaken to optimise these techniques, production of fingerprint dusting powder with small, well dispersed and rounded particles have yet to be reported. Additionally, many of the varied powders introduced mainly use synthetic precursors, including titanium dioxide and silica powders (Becue *et al.*, 2007; Theaker *et al.*, 2008; Arshad *et al.*, 2015; Moret *et al.*,

2016). The preparation of precursors used for the commercial and previously proposed product synthesis consumes significant cost and energy. Enhancement of the sensitivity was proposed to be possible but at a higher cost than the current methods. Moreover, the techniques that have been proposed have limited field applicability and eliminate possible recovery of other evidence present on the substrate bearing the fingermark (Sodhi and Kaur, 2017).

Techniques such as multimetal deposition (MMD) and vacuum metal deposition have limitations such as extremely narrow pH conditions for effective development, carcinogenic properties, costly and destructive in nature (Gao *et al.*, 2009). Functionalisation of nanoparticles may increase the precision of the particle interaction with a specific component of the residue (Leggett *et al.*, 2007), but obstacle arises when the presence of a targeted component is insufficient. The aqueous nature of the functionalised nanoparticles contaminates the surface and destroys the fingermark residue. Contamination makes it unlikely for the retrieval of other forensic evidence such as drug detection or deoxyribonucleic acid (DNA) extraction. As a result, these techniques are often used as a last resort of attempt at fingermark recovery.

The widespread interest in nanoparticles arises due to several inherent advantages as compared to conventional techniques on account of their small size that enables high-resolution fingermark development. Besides, their quantum confinement property enables the production of luminescent prints as well as a wide range of surface modification potential that targets specific component (Moret *et al.*, 2016). Generally explored nanoparticles for fingermark detection include gold and silver nanoparticles as well as metal oxides, such as titanium dioxide, aluminium oxide and zinc oxide (Stauffer *et al.*, 2007; Chadwick *et al.*, 2012; Sodhi and Kaur, 2017). However, most

nanoparticles has weak or no luminescence at all which confine their applications to light coloured surfaces to provide sufficient contrast.

Conferring luminescent property to these nanoparticles although possible, requires a tedious protocol and still limited to non-porous surfaces only. Use of quantum dots (QD) is also limited because surface functionalisation to improve selectivity comes at the expense of altering the structural and luminescence properties. Hence, despite the collective efforts of introducing nanoparticle-based fingermark detection techniques, each technique lack either one of the following factors; small size, optical properties or surface modification.

One type of nanoparticles that possesses all the three factors combined in one entity is the silica nanoparticles (SiNPs). Nonetheless, application of SiNP for fingermark development has not been strongly researched until recently. SiNPs consists of a porous matrix made up of siloxane bonds, with an outer layer of silanol bonds which are highly reactive with alkoxysilanes offering limitless functionalisation capacity. In addition, dye molecules can be easily entrapped into the porous matrix conferring photoluminescent properties to the SiNP. Copious synthesis methods exist for fabrication of SiNPs, but Stober's synthesis and reverse microemulsion techniques are the most generally employed techniques. Stober's synthesis offers bulk production meanwhile reverse microemulsion offers better control over the size and surface of the SiNP nevertheless with a lower yield. Additionally, these techniques exploit synthetic precursors such as tetraethyl orthosilicate (TEOS).

A few reports regarding the application of SiNP synthesised via these routes using expensive synthetic precursors for latent fingermark development has been previously reported (Theaker *et al.,* 2008; Reip *et al.,* 2010; Moret *et al.,* 2016). In addition to

the higher cost and energy consumption for the production of the synthetic precursors utilised, these techniques produced highly agglomerated nanostructured SiNPs in powder form. The SiNP suspension upon drying was also reported to be crystalline in nature, translating into the fact that the particles possess lattice structure which is unsuitable for fingermark development according to much previous literatures (Wilshire, 1996; Sodhi and Kaur, 2001).

Abundant research has been dedicated to extracting silica from rice husk (RH) in amorphous or crystalline form. Nevertheless, these research prioritised extraction of highly porous SiNP in the smallest size, regardless of the agglomeration state primarily to be applied as fillers, absorbents or drug carriers (Hassan *et al.*, 2014; Noushad *et al.*, 2014; Abu *et al.*, 2016). Prior to this research, silica extracted from RH has never been applied for the development of fingermark, which require particles of different morphology such as small sized, spherical and minimally agglomerated.

The goal of this study was to address lack of fingerprint developing products that comprises of well-dispersed nanoparticles that have specific shape and size that simultaneously exhibit higher selectivity and sensitivity to fingermark residue. Other than that, the nanoparticles were produced from agricultural waste, RH, which not only serve to recycle waste products but also to minimise manufacturing cost and health hazard to the users. Lowering the cost of the products will significantly improve the reach of the technology to all potential customers. Hence, enabling easy incorporation into routine forensic investigations.

1.4 Aim and objectives

The principal aim of this research was to fabricate nanoparticles from RH and to assess their use as potential latent fingerprint developing powders and reagent with increased selectivity and sensitivity.

Specific objectives of this research were:

1) To establish an optimised extraction procedure of pure SiNP and carbon nanoparticle (CNP) from rice husk ash (RHA) for production of nanoparticle powders ideal for the development of latent fingermark on dark or light non-porous and semi-porous surfaces and their characterisation using various imaging and analytical techniques.

2) To formulate nanoparticle reagent (NPR) using SiNP powder for the development of fingermark on wet and sticky surfaces.

3) To produce multicoloured SiNP powders with photoluminescence property using natural or synthetic dyes for the development of latent fingermark on multicoloured and patterned surfaces.

4) To investigate the effectiveness of the nanoparticle powders and reagent in comparison to commercial products on fresh and aged fingermarks in controlled laboratory settings as well as in field study with the Royal Malaysian Police.

1.5 Scope of research

This research was conducted in a few phases, which are outlined in **Figure 1.1.**

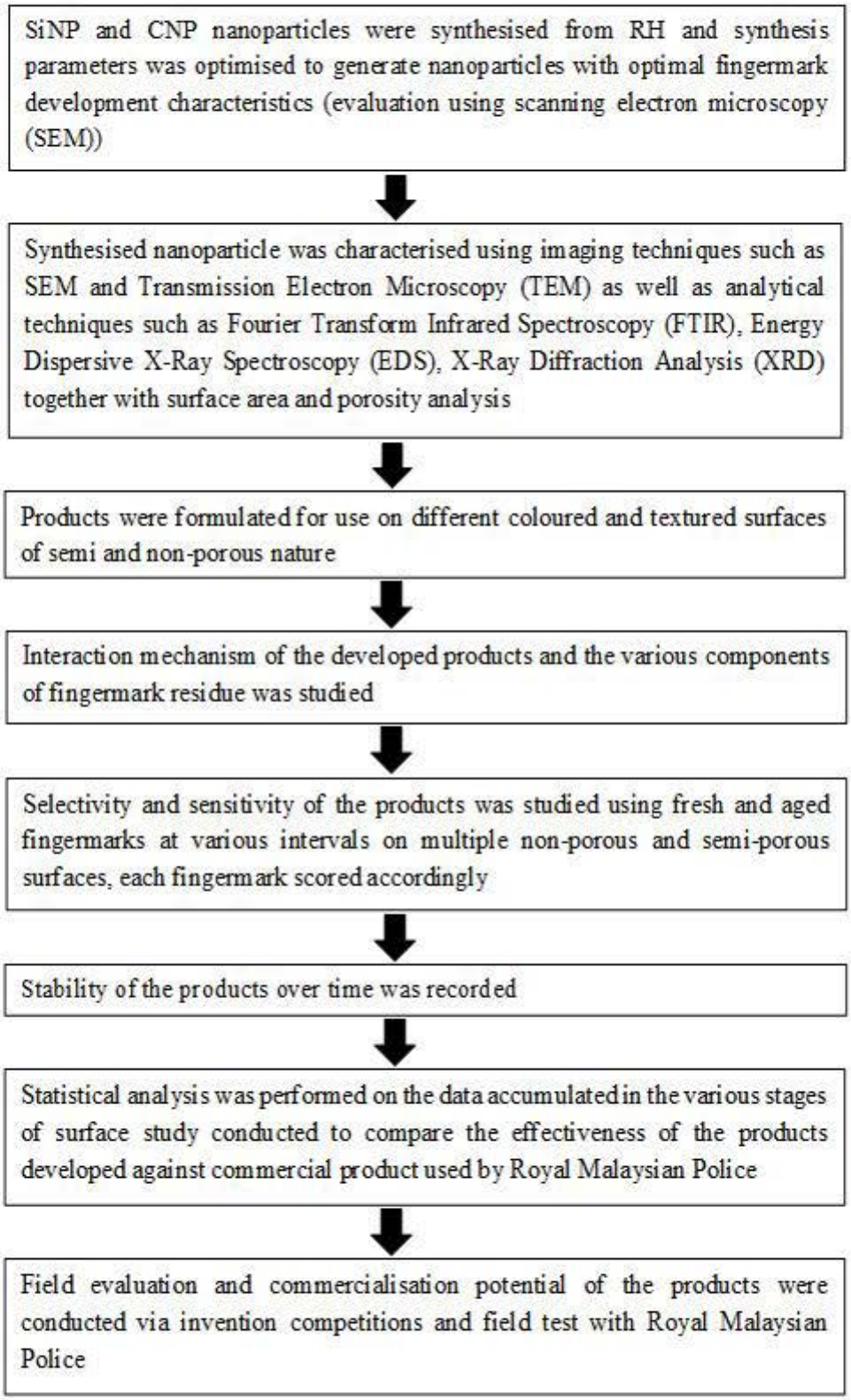

Fig. 1. Outline of the scope of research

1.6 Thesis outline

The first chapter elaborates the research background, problem statement, the gap of knowledge as well as the aims and objectives of this research. The second chapter of this thesis encompasses an elaborate definition of the terms used throughout this thesis and the literature review of the key components of this thesis. The third chapter encompasses the extraction of silica from RH and subsequent synthesis of SiNP with optimal characteristic for fingermark development.

Chapter 4 illustrates the application of the synthesised SiNP powder as dry and wet powder suspension for the development of fingermarks on various non-porous and semi-porous surfaces, studying the interaction, selectivity, sensitivity of the powder and reagent. Chapter 5 describes the extraction of natural dye pigments and doping them into the SiNP powder in order to produce fluorescent SiNP powders that provide better contrast on multi-coloured surfaces.

Chapter six depicts the synthesis steps of spherical CNP from RH and the subsequent application along with the sensitivity and selectivity analysis on various non-porous and semi-porous surfaces. The fingerprint kit comprised of the white and multicoloured SiNP powder, black CNP powder and NPR (ECO^{fp} Fingerprint Kit) is introduced in this chapter as well. Chapter seven discusses the conclusions, limitations and future studies recommendations for this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanoparticles

Nanoparticles research are a fascinating branch of science. A scientifically correct definition of nanoparticle has yet to be provided (Boverhof *et al.*, 2015). Most widely accepted definition of the nanoparticle is an individual entity having all three-dimensional measurement or at least one dimension measuring in the range of 1 to 100 nm (Moreno-Vega *et al.*, 2012). Although the range of 1 to 100 nm is used to define nanoparticles, there is no evidence supporting begin and abrupt ending of physical and chemical attributes of nanoparticles below and above this range. For example, many properties characteristic of nanoparticles still continues well above the upper limit of 100 nm (Lidén, 2011; Maynard, 2011).

Therefore, a more inclusive definition of nanoparticles has been proposed considering the fact that particle size distribution alone is not enough to provide an accurate definition. Authorities such as Taiwan Council of Labour Affairs and European Commission have set two conditions to be met for nanoparticle inclusion. The material either possesses one or more external dimension in the nanoscale range or beyond this range but exhibits nanoscale properties such as increased chemical reactivity (Health-Canada, 2011; Lidén, 2011; Taiwan, 2012).

Another report suggested the use of the following three categories to define different levels of nanomaterial. Category one is the nanomaterial with a mean particle size larger than 500 nm. In the category, the lower limit of size would most likely be above the designated 100 nm cut-off. Thus, further investigation regarding nanoscale properties is required for inclusion in nanoparticle range. Category two is where the

mean particle size lies between 500 nm and 100 nm, where it is more than likely that part of the size distribution will be lower than 100 nm. Hence, that material may be considered nanomaterial and more detailed characterisations are required to do the correct determination. The third category is when the mean particle size falls in between the range of 1 and 100 nm and are considered nanomaterial (Auvinen *et al.*, 2010).

Advantages of using nanoparticle for fingermark development have been widely researched (Becue *et al.*, 2007; Moret *et al.*, 2014). SiNP in the range of 400 to 500 nm has been reported to develop fingermark with sufficient clarity (Theaker *et al.*, 2008). Another study utilised nanostructured zinc oxide with a flower-like structure with aggregated dimensions measuring up to one micrometre for fingermark development. The developed fingermarks exhibited clear ridge detail (Choi *et al.*, 2008a). Alternatively, dye-doped nanophosphors with the dimension 300 to 500 nm that were also investigated for fingermark development reported positive outcome for extremely dry fingermarks (Reip *et al.*, 2010).

2.1.1 Nanoparticle synthesis

Synthesis of nanoparticles can be categorised into two most basic methods that are either the top-down or the bottom-up approaches. The precursor material used for these techniques can either be of synthetic or natural in origin (Noushad *et al.*, 2012; Moret *et al.*, 2014). The purity of the final product and particle size distribution are ultimately governed by the nature of the manufacturing process and any integral purification steps involved, such as acid digestion or calcination for silica extraction from RH (Vaibhav *et al.*, 2015). The top-down or the physical method of nanoparticle creation is the fine division of the bulk element into their respective nanosized counterpart (Balasooriya *et al.*, 2017).

The bottom-up approach is a more commonly adapted chemical route of nanoparticle synthesis. Nucleation of the specific atom and subsequent or simultaneous aggregation of the atoms forms nanoparticles of the required size (Merza *et al.*, 2012; Rahman and Padavettan, 2012; Polte, 2015). The basis of the wet chemical reduction is the formation of an aqueous solution containing the element of interest and reducing the ions into atoms using any reduction agents (Sharma *et al.*, 2009). Sometimes a catalyst or stabilising agents accompany the process to aid in the formation of specific shape and size distribution of such nanoparticles via electrostatic repulsion or stearic stabilisation (Abid *et al.*, 2002). For example, SiNP can be synthesised by reducing SS_{rh} prepared from RH silica (Lee *et al.*, 2017).

There are a few methods to control the size and shape of the particles formed during synthesis mainly by governing the different aspects of the nucleation and growth of the particles. It was observed that the addition of different acids and solvents affected the properties of SiNP formed from SS_{rh} (Noushad *et al.*, 2012). The stoichiometric ratio of the synthesis process is very important to control the pH, amount of reactants available and the time taken for the reaction to fully complete directly affecting the particle size (Wang *et al.*, 2010b). Capping agents such as surfactants offer control over particle size by coating the generated particles to form an electrostatic barrier to avoid further growth and also simultaneously stabilising the particles from agglomerating (Jana *et al.*, 2001).

The time taken for the reaction to complete has an inverse effect on the size distribution of the particles. As the time taken for the reaction is increased the gap between the newly formed nucleus and the first formed nucleus is multiplied. As a result, the particle size distribution will be huge because by the end of the process the first formed nucleus will acquire large growth as time increases (Jimenez-Ruiz *et al.*, 2015).

Separation of the nucleation and growth process, for example, the Turkevich method of gold nanoparticle (GNP) synthesis, can afford full control of the particle size. The nucleation of gold atoms are conducted separately to produce particles of 20 nm size and then seeded into a growth media in a specific ratio to produce particles double the size of the seeded nucleus (Kimling *et al.*, 2006).

Control over the number of reactants can be achieved by creating an emulsion containing the aqueous solution of the element, otherwise known as micelles. Dispersing tiny droplets of the elemental aqueous solution in the emulsion will limit the provision of the reactants thus, effectively limiting the growth of the particles (Finnie *et al.*, 2007). Alteration to any of the factors of nucleation and growth can lead to uncontrolled growth as well as large particle formation (Schnetz and Margot, 2001). The same principle can be applied to control the formation and aggregation of SiNP from RH.

2.1.2 Nanomaterial characterisations

A newly synthesised nanomaterial may be characterised using analytical instruments to understand its intrinsic structure and properties (Murdock *et al.*, 2008). New nanomaterial may be characterised by its morphological, structural and optical features as well as particle size and surface area analysis (Lu and Hsieh, 2012). Morphological characterisations warrant great attention because of its influence on various properties of the nanomaterial. Microscopic techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), polarised optical microscopy and atomic force microscopy offers a remarkable pathway to gleam morphological information of the nanomaterial at an elemental level. SEM offers information on the

surface level of the particles while TEM provides information on the bulk material from very low to higher magnifications (Zhou *et al.*, 2007; Egerton, 2016).

Structural properties of a nanomaterial can be obtained using instruments such as X-Ray Diffractometer (XRD), Energy Dispersive X-Ray Spectrophotometer (EDS), Fourier Transform Infrared Spectrophotometer (FTIR), X-Ray Photoelectron Spectrophotometer (XPS), Brunauer-Emmett-Teller (BET) and particle size analysis. Each instrument provides different structural information. XRD reveals the crystallinity and phase, EDS; the elemental composition, FTIR: structural bonds and material signature and BET for the total surface area determination. XPS is a more sensitive way of determining the exact elemental ratio and bonding nature of the elements (Als-Nielsen and McMorrow, 2001; Schneider, 2011; Eckert, 2012).

Optical techniques are aimed to determine the absorption, reflectance, luminescence and phosphorescence properties of a nanomaterial. Analytical instruments such as Ultraviolet-Visible (UV-Vis) and fluorescent spectrophotometers can provide this information (Khan *et al.*, 2017). This is imperative to determine the interactions of the nanomaterial with the electromagnetic energy so that they can be engineered to fit the purpose of use.

2.2 SiNP

Silicon is the second most abundant element on the Earth's crust and due to its strong bond with oxygen atoms, it rarely exists as a pure element (Bansal *et al.*, 2006; Meng-Hao *et al.*, 2012; Liu *et al.*, 2013). Silicon often exists as crystalline silica (silicon dioxides) or synthetic amorphous form (silicates). Silica, a polymer of silicic acid consists of base units of the tetrahedral form of interlinked SiO_4 (Jal *et al.*, 2004).

Crystalline silicon is widely used in metallurgy, silicone synthesis and also in the

semiconductor industry. On the other hand, amorphous silica have unique properties that makes them exploitable in the ceramics, rubber fillers, pharmaceutics, dental materials, biomedical, absorbent, nanoelectronics, photonics, biotechnology, energy harvesting, composite fillers, thermal insulators and thixotropic agents (Kamath and Proctor, 1998; Liou, 2004; Choi *et al.*, 2008b; Becue *et al.*, 2011; Rafiee *et al.*, 2012; Liu *et al.*, 2013; Noushad *et al.*, 2014).

Manufacturing of pure silica is energy-intensive when conventional raw materials are utilised (Mittal, 1997; Kalapathy *et al.*, 2002). Most common SiNP precursors are silicon alkoxides or silicates which in turn are synthesised from raw material like sand through smelting method (Kalapathy *et al.*, 2000; Jal *et al.*, 2004; Shen *et al.*, 2014). This process requires high energy, high-temperature, high pressure and also strong acidity (Bansal *et al.*, 2006).

Plants have natural silica synthesising system that converts water-soluble silicic acid seeped from the ground into amorphous silica by precipitation and polymerisation (Yoshida *et al.*, 1959; Lu and Hsieh, 2012). Silicon transported from the root through xylem as silicon complex are accumulated in the plants in solid form creating phytoliths (intracellular and extracellular silica bodies) (Shen *et al.*, 2014; Sivasubramanian and Kurcharlapati, 2015). A few examples of groups of plants containing natural silica are Myrtaceae, Casuarinaceae, Cyper- aceae, Gramineae, Palmae, Pinaceae, Taxodi-aceae and Equisetaceae (Shen, 2017).

Amorphous silica has been successfully extracted from rice plant, groundnut shell, sugarcane bagasse, corn cob ash, coconut shell and bamboo leaves (Rafiee *et al.*, 2012; Noushad *et al.*, 2014; Aminullah *et al.*, 2015; Sivasubramanian and Kurcharlapati, 2015; Wang *et al.*, 2015). Rice (*Oryza sativa)* which comes under the family

Gramineae, contains a high amount of silica especially in the husks (Yoshida *et al.*, 1959; Liu *et al.*, 2013). Yearly tons of RH is produced as by-products of rice, the world's second most produced crop species in countries such as China, Malaysia, Arab, Republic of Korea and India (Park *et al.*, 2003; Lu and Hsieh, 2012; Liu *et al.*, 2013). Global rice production stands around 466 million tons as of the year 2010/2011 and RH account for one-fifth of it (Rafiee *et al.*, 2012; Gu *et al.*, 2013).

One of the pioneering reports indicated the presence of amorphous hydrated silica in rice plants using FTIR analysis of untreated RH (Yoshida *et al.*, 1959). Other studies demonstrated that the sheaths contain the highest amount of silica about 17.50% in comparison to silica content in roots, stems and leaves (straw) (Lanning, 1963).

RHs has a very hard exterior surface and are mainly made up of the tightly interlocked lemma and palea, both having similar morphology. The epidermal surface of the lemma is arranged in linear ridges punctuated with prominent conical protrusions with hair like papillae extending from the surface at some intervals. The outer surface of the RHs are highly undulated and two thick layers of walls underlie the outer epidermis (Park *et al.*, 2003). Silica is heterogeneously distributed on the upper and lower surface of the RHs, in the range of micrometre-sized particle of various morphology (Bansal *et al.*, 2006). Amorphous nature of these silica makes them highly soluble and thus extractable at alkaline conditions in lower temperatures (Kalapathy *et al.*, 2002).

RH is primarily used as a fuel source and bedding for animals with limited application observed in the industrial field (Park *et al.*, 2003; Bharadwaj *et al.*, 2004). The high calorific value of RH renders it as an excellent source for heat generation and production of natural gases (Ahmed *et al.*, 2008). The primary disposal methods of RH is by burning. This causes air pollution through the release of a large number of

greenhouse gases or by stacking in farmland that wastes space (Noushad *et al.*, 2014). At the same time, RHA is also dissipated into the air causing silicosis syndrome in exposed residents (Tadjarodi *et al.*, 2012; Vaibhav *et al.*, 2015).

The hard exterior of the RH due to high silica content renders them immune to bacterial decompositions (Noushad *et al.*, 2014). The increase in the fossil fuel price has prompted the manufacturers to switch to use RH as a fuel source in industrial boilers. The burning of RH releases crystalline silica (cristobalite) into open air that is classified as a hazardous compound that causes cancer (Yang *et al.*, 2015).

Exploitation of RH for commercial purposes are being extensively explored to synthesise nanomaterial at a much lower cost. Extraction of cellulose and silica from RHA have been widely researched, to produce silica using the low-cost method from a sustainable source. This also reduces the ecological impact of accumulating RH and prevents air pollution caused by burning of this waste material (Rafiee *et al.*, 2012; Carmona *et al.*, 2013; Vaibhav *et al.*, 2015).

Silica particles synthesised from agricultural waste sources are highly porous and possesses high surface area. They are found to be a useful raw material in ceramics, electronics, catalysis, pharmaceutics, dental materials and forensics (Choi *et al.*, 2008b; Moret *et al.*, 2014, 2016; Marin *et al.*, 2015). The composition of RH varies according to the geographical location, type of paddy, climate condition and soil chemistry. A rough composition as reported in earlier studies is summarised in **Table 2.1**.

Table 2.1 The composition of RH: Elemental and organic constituents of RH (Soltani *et al.*, 2015)

Composition of RH	Percentage
Elemental composition	
Carbon	37.05%
Hydrogen	8.80%
Nitrogen	11.06%
Silica	9.01%
Oxygen	35.03%
Contents of RH	
Hemicellulose	24.30%
Cellulose	34.40%
Lignin	19.20%
Ash	18.85%
Others	3.25%

2.2.1 SiNP synthesis

The six routes of SiNP synthesis from synthetic precursors and RHs are vapour-phase reaction, thermal decomposition, chemical digestion, precipitation, sol-gel technique and fungus mediated transformation (Gorji and Ghasri, 2012; Noushad *et al.*, 2012; Rahman and Padavettan, 2012; Shekar *et al.*, 2012; Yue *et al.*, 2013; Moret *et al.*, 2014). Vapour-phase reaction involves an inert gas such as argon carrying the silica precursor allowing reaction with the vapour of solvents to produce SiNPs. The size of the particles can be controlled by controlling the dilution of the carrier gas (Yue *et al.*, 2013).

Thermal decomposition or chemical digestion of RHs can produce SiNPs with various purity levels (Hanafi, 1980; James and Rao, 1986; Conradt *et al.*, 1992; Krishnarao *et al.*, 2001). The sol-gel process utilises soluble molecular precursors transformed into atomic seeds of an element and followed by polymerisation or condensation subsequently forming larger particles (Coradin *et al.*, 2006). Precipitation of SiNP from sodium silicate generated from RH (SS_{rh}) solution can also be realised by inhibiting gel growth and promote polymerisation to form silica powders. Conditions

of the precipitation may be altered by the addition of solvents, change in pH or by creating microemulsion state to control particle growth (Jal *et al.*, 2004).

Reverse microemulsion or water-in-oil microemulsion method can be defined as a thermodynamically stable and transparent solution containing water, oil and surfactant. The solution contains tiny micelles or droplets of nanosized water entities dispersed in oil. Surfactant functions to form a barrier like a wall around the liquid droplets creating nanosize reactor wells that allow limited reaction of nanoparticle formation and avoids molecular aggregation (Bagwe *et al.*, 2004; Naka *et al.*, 2010).

Another synthesis method is the combustion of precursors in the form of gas, liquid and solid which are injected into the burner and instantaneously reacted at high-temperature to form product molecules. This molecule then undergoes subsequent reactions and finally coalesce to form larger aggregates (Shekar *et al.*, 2012; Yue *et al.*, 2013). RH can also be digested using certain fungus to extract and transform amorphous silica into a crystalline state (Bansal *et al.*, 2006).

As a greener alternative, high content of silica in RH have been exploited and explored as a possible source for SiNP, silicon carbide, silicon nitride, sealon and zeolite synthesis (Noushad *et al.*, 2012, 2014; Gu *et al.*, 2013; Zulkifli *et al.*, 2013; Shen *et al.*, 2014; Marin *et al.*, 2015). Over the years, more studies have been centred on the optimisation of each governing parameters of SiNP production from RH. Copious studies have been undertaken to produce purer silicon compounds by acid and alkali leaching as well as modulating RH sintering temperatures (Kalapathy *et al.*, 2000, 2002; Della *et al.*, 2002; Zaky *et al.*, 2008).

Extraction and purification of silica from RH must be tailored to the intended use of the product. SiNP can be extracted in three forms; crystals, gels and powder.

Modifying the stability of the solution by controlling the electrical charges can be used to modulate the final form of the SiNP. Polymerisation or repulsion of particles can be fluctuated by decreasing or increasing the surface charges respectively. Various parameters such as pH and solvents can be used to alter the electrical charges resulting in the formation of SiNP of different characteristics (Le *et al.*, 2013).

2.2.1 (a) Extraction of SiNP through thermal decomposition of RH

The crudest form of silica with low purity can be extracted by thermal treatment of RH. Burning the RH at elevated temperature is undoubtedly the easiest method to extract silica. However, the side effects of the method such as pollution have induced scientists to implore a relatively benign manner of silica extraction (Adam *et al.*, 2011; Zulkifli *et al.*, 2013). The burning of RH at 450℃ or above retains the trace metal impurities that interfere with the final characteristics of the amorphous silica (Lu and Hsieh, 2012). The presence of trace metal impurities affects the purity of the silica, causes surface melting and crystallisation of silica during heat treatment and also carbon fixation in RHA. Quality, colour and state of the RHA are dependent on factors such as pretreatment with chemicals, ashing temperature and heating rate (Rafiee *et al.*, 2012).

RHA with different levels of purity and crystallisation can be obtained by modulating the heating rate and temperature as well as chemical pre-treatment. Physicochemical changes of the RH after chemical and heat treatments can be monitored using analytical instruments such as surface area analyser, XRD, dynamic thermoanalytical techniques and FTIR (James and Rao, 1986). RHA which mainly contains silica can be produced when RH is heated at a high temperature above 500℃. The increasing and decreasing pattern in the total surface area together with the crystallinity of the

RHA as the heating temperature was increased from 500 to 1400℃ offers insight into the morphological changes RH undergoes (Hanafi, 1980).

Total surface area of the RHA increased when heating temperature was increased from 500 to 600℃, indicating break down of silica into SiNP. Then a decreasing trend was observed when the temperature was further increased to 900℃, representing either agglomeration of the smaller particles or size growth (Ibrahim and Helmy, 1981). A sudden plunge in the total surface area and change in crystalline state can be observed at a heating temperature beyond 900℃ indicating amorphous silica began crystallising (Vaibhav *et al.*, 2015). Further increase in heating temperature beyond 1400℃ leads to a sudden increase in the surface area indicating the formation of smaller crystals (Hanafi, 1980; Fernandes *et al.*, 2017).

Thermal decomposition analysis sheds light on the chemical changes that RH undergoes as the thermal treatment is conducted. Three major decomposition peaks at 373K, 533K and 735K can be observed during the heat treatment of RH. The first peak was attributed to the loss of sorbed water (James and Rao, 1986). The second major mass loss was attributed to the breakdown of the cellulose and lignin constituents through glowing combustion (Liou, 2004; Fernandes *et al.*, 2017) and the final exotherm indicated combustion of product gases or from lignin decomposition as postulated by another researcher (Abu *et al.*, 2016).

A complete combustion was favoured in an oxygenated atmosphere in comparison to the nitrogen-saturated atmosphere (James and Rao, 1986). Heating RH or black RHA obtained from rice mill at 500℃ for 8 hours or at 700℃ for 6 hours produced white amorphous RHA with 94.95 % purity but with drastic decrease in total surface area

from 177 m^2/g to 54 m^2/g after heat treatment owing to the agglomeration effect and diminished porosity (Della *et al.*, 2002).

Silica of higher purity can be extracted from RH by removal of the trace metal impurities using chemical treatment pre or post to heating treatment. Volumes of research have been dedicated to determining the optimal type and concentration of the chemical for RH treatment as well as the duration of chemical and heat treatment. The treatment was aimed to produce pure SiNP with small size and high surface area. To date, the literature shows consensus on pre-treatment of RH using hydrochloric acid (HCl) before heat treatment to produce the purest silica possible with the highest surface area and smallest size. Prior to reaching this conclusion, various other chemicals have been tested for the chemical treatment of RH to completely remove trace metal impurities. HCl, nitric acid, sulphuric acid and NaOH were among the chemicals tested for this purpose (Mishra *et al.*, 1985; Chakraverty *et al.*, 1988; Conradt *et al.*, 1992; Abu *et al.*, 2016).

Pre-treatment of RH using NaOH did not only remove trace metal impurities but also silica. This was due to amorphous silica has a high solubility in alkali medium (Conradt *et al.*, 1992). Treatment of RH using boiled solutions of HCl, sulphuric acid, phosphoric acid, nitric acid and other acid is effective in breaking down cellulose and lignin components as well as removing metallic impurities. Acid component reacts with the metal to form soluble compounds that can be washed out from the solid residue (Sun and Gong, 2001).

Previous findings have reported that HCl pre-treated RH produces silica of the highest purity of approximately 99.86% after heat treatment followed by sulphuric and nitric acid pre-treated RH at approximately 99% purity (Yalçin and Sevinç, 2001; Wang *et*

al., 2012; Ghorbani *et al.*, 2015; Abu *et al.*, 2016). Theoretically, the nitric acid should be able to remove trace metal impurities effectively in comparison to HCl because metal nitrates are more soluble than metal chlorides (Speight, 2005). However, in this case, HCl was reported to be more effective in removing trace metal impurities than nitric acid. This might be because nitric acid reacts with cellulose present in the RH forming nitrocellulose reducing its reactivity with trace metals (Baumann *et al.*, 1982). HCl does not react with cellulose but helps with acid hydrolysis of cellulose into oligosaccharides (Fan *et al.*, 1987).

Another study claimed that production of highly pure RHA was possible by subjecting raw RHA formed from combusting RH at 500℃ to acid treatment for two hours. However, the authors did not conduct an elemental analysis of the product to support their claim (Mishra *et al.*, 1985). This finding was not in agreement with a later report which stated that the RHA produced without prior acid treatment remained light brown concurrent with other subsequent research (Chakraverty *et al.*, 1988; Real *et al.*, 1996). A dramatic drop in the total surface area occurred if the acid leaching was conducted after ashing. This phenomenon was attributed to the interaction of potassium ion and silica. Potassium ion causes surface melting when RH was subjected to sudden heating trapping the carbon particles in the ashes (Krishnarao *et al.*, 2001; Rafiee *et al.*, 2012).

The ash produced retained the shape of the RH grains when viewed under SEM but soft grinding of the ash results in a fine powder (Liou, 2004). This further offered to prove that silica was homogeneously distributed on the surface of RH since the ash contains 99% ± silica. The fine silica ash observed under SEM revealed SiNP smaller than 100 nm whereby the particles exhibited a high level of agglomeration (Conradt *et al.*, 1992).