ORIGINAL ARTICLE

Green Chemistry Synthesis of Nanostructured Zinc Oxide Powder Using *Azadirachta indica* Extract for Latent Fingermark Development

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ABSTRACT

Introduction: Application of nano-engineered fingerprint dusting powders has been a recent trend to achieve latent fingermark development with superior ridge clarity. As such, efforts have been made to utilise natural resources to increase the sustainability of these emerging nano-engineered powders. Lithium-doped zinc oxide, primarily used as white pigments, have been previously applied to latent fingermarks with success. In the current study, nanostructured zinc oxide, synthesised using neem extract as the reducing agent, was evaluated for fingermark development on non-porous surfaces. **Methods:** The reduction of zinc nitrate hexahydrate was facilitated by neem extract, prepared by boiling neem leaves in distilled water. The thick yellow paste recovered was calcined in the furnace to produce a light yellow powder. Physicochemical composition of the powder was determined using microscopic and spectroscopic instruments. The effectiveness of the powder was tested on natural fingermark deposited on several non-porous surfaces. **Results:** Nanostructured zinc oxide with particle size ranging in between 1 to 3 μm consisting of highly aggregated spherical particle with less than 100 nm dimensions were synthesised. Developed fingermarks revealed excellent ridge details and contrast on dark coloured surfaces. Studying the fingermark closely under scanning electron microscope displayed selective distribution of particle on the ridges of the fingermark residue and very minimal deposition on the fingermark valleys. **Conclusion:** Nanostructured zinc oxide fabricated using green chemistry approach can be applied for the development of fingermark. Nevertheless, future works can be undertaken to enhance particle dispersity and to confer strong photoluminescence to the zinc oxide nanoparticles.

Keywords: Green chemistry, Zinc oxide nanoparticles, Fingermark, Neem leaves

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INTRODUCTION

Fingermarks still remains the best means of perpetrator identification in crime scenes as much as powder dusting remains the most reliable and heavily utilised fingermark development technique. Advancement in nano-engineering of powders has led to the production of far more superior fingerprint dusting powders capable of developing fingermarks with a higher degree of clarity. Nevertheless, conferring luminescent properties to the powders in order to enhance contrast is a persisting challenge. The primary issue being the use of toxic dyes to confer luminescent makes the powders less user-friendly.

Previously, lithium doped zinc oxide nanostructured powder was explored as a suitable alternative for fingerprint dusting powders. The synthesised powder contained powder particles which had stacked petals in a flower-like arrangement in the dimensions of one to two micrometres. Authors reported that using the powder in wet particle suspension technique yielded better clarity than the powder dusting technique. Nonetheless, the fabricated powder exhibited good performance with enhanced luminescence observed at 587 nm due to the doped lithium (1).

A green route of zinc oxide synthesis using plant extract was introduced nearly a decade ago as an attempt of more ecological, cost saving, biocompatible, harmless and green approach (2). Sustainable synthesis at times involves the utilisation of natural existence such as plants, bacteria, fungi and algae. Natural extracts have the capacity to act as reducing and capping or stabilising agent (2). Using natural extracts is not only eco-friendly but also does not involve the use of costly instruments and precursors while producing highly pure and product free of impurities. Inspired by the synthesis of widely researched green synthesis routes of the silver nanoparticle using plant extracts, bacteria, fungi and enzymes, Sangeetha et al, (2011) (3) pioneered the green synthesis of nanostructured zinc oxide using Aloe vera leaf extract.

These researchers extracted broth from aloe leaves and used it to reduce zinc nitrate. They observed a hundred per cent conversion and a high rate of synthesis when more than 25 % concentration of aloe broth was used. Nevertheless, the chemical synthesis only resulted in a fifty per cent conversion when the same time length was used. The size of the nanostructured zinc oxide synthesised using aloe extracts was about 35 nm whereas the chemical method produced particles of 60 nm on average (3). Scanning electron microscopy (SEM) images of nanostructured zinc oxide displayed a high level of agglomeration and irregular shape. The synthesis also takes a very long time of six to seven hours to achieve complete conversion.

Since then many green synthesis techniques of zinc oxide nanoparticles have been attempted using varied plant extracts such as Calotropis procera (4), seaweeds (5), Citrus aurantifolia (6), Azadirachta indica (7–9), Emblica (7), Peperomia pellucida, Celosia argentea (10), Passiflora foetida (11), Coriandrum sativum (12) and Acalypha indica (13). Singh et al, (2011) (4) used latex of Calotropis procera as a catalyst, however, this two hours synthesis method still requires the addition of sodium hydroxide. Proposed synthesis method using seaweeds, Corriandrum sativum, Azadirachta, Emblica Officinalis, Acalypha indica also faced similar drawbacks of involving sodium hydroxide and irregularity in the particle shape and size of the derived zinc oxide (5,7,12–14). Despite that, other researchers have proven that synthesis can be carried out without the addition of sodium hydroxide and at a relatively shorter time period (6,15–17). A detailed review of the green synthesis of nanostructured zinc oxide has been published recently (2).

Azadirachta indica (neem leaves) is a tropical tree commonly found in southeast countries and widely available plant in Malaysia. The medicinal properties of neem leaves are highly recognised in Ayurvedic medicine due to its healing versatility (18). It has strong antibacterial, antifungal, antidiabetic, antiviral and contraceptive properties (7). The various medicinal uses of these plants arise from the content of the plant such as alkaloids, flavonoids, steroids, carbohydrates, terpenoids and glycosides compounds (8,18). Previously, the use of this extract for the reduction of zinc nitrate hexahydrate has been reported (18). In this research, nanostructured zinc oxide synthesised following previously reported technique has been applied for latent fingermark development on several non-porous surfaces. The primary aim of this research was to exploit the nanostructure of the zinc oxide and its photoluminescence to enhance the clarity and contrast of the fingermark developed on non-porous surfaces.

MATERIALS AND METHODS

A green chemistry approach was applied, whereby the reduction of zinc nitrate hexahydrate was performed using neem leaves extract, according to previous literature (18). Cleaned neem leaves (50g) were boiled in 250 mL of distilled water at 60^{o}C for 20 minutes and the mixture was filtered to obtain a light yellow filtrate. Subsequently, 2 g of zinc nitrate hexahydrate crystal was dissolved in 20 mL of the neem extract solution and was heated at 80^{o}C under constant stirring until a deep yellow coloured paste was obtained. The paste was transferred to porcelain crucible and calcined in the furnace for 2 hours at 400^{o}C to produce light yellow coloured ZNP powder.

Characterisation of ZNP

Fabricated nanostructured zinc oxide was characterised using several analytical instruments to determine its morphological and chemical properties. The surface topography and the structure of particle were determined using topographical analysis based on sample interaction with low energy electron beam (5.0 kV acceleration voltage). The micrographs were recorded using SEM (Quanta FEG 450, FEI Czech Republic) after sputter coated with gold using Leica EM SCD005 Coating System to assist sample conductivity. Observation of images was performed at an approximate distance of 9 to 10mm working distance. Elemental analysis of the samples was performed using Xmax 50mm2 Energy Dispersive X-Ray Spectroscopy (EDS) (Oxford, United Kingdom). Elements present in the sample were determined by exploiting characteristic x-rays emitted by the samples. Analysis of the molecular bonding in the neem extract, zinc nitrate hexahydrate and nanostructured zinc oxide was performed using infrared (IR) spectroscopic analysis using Tensor 27 Fourier Transform Infrared Spectroscopy (FTIR) spectrometer by Bruker Corporations, United Kingdom. Samples were ground along with potassium bromide and pressed into pellets and sample interaction with infrared radiation from 4000 to 400 cm-1 was recorded.

Fingermark development

The subject was required to wash hand without soap and continue with regular activity for 30 minutes. Fresh natural fingermarks without any additional sebaceous grooming were deposited on clean non-porous surfaces; black acrylic plastic, black glass and metal plate. These fingermarks were developed using the fabricated zinc oxide powder and regular SIRCHIE white powder to determine the efficacy of the powder. Fingermarks developed on the acrylic plastic surface using zinc oxide and SIRCHIE white powders were viewed under scanning electron microscopy and ultraviolet light to ascertain the clarity and contrast of the ridges.

RESULTS

The thick light yellow extract was obtained from boiling the neem leaves and the extract turned into a light yellow paste after adding zinc nitrate hexahydrate.

Nanostructured zinc oxide observed after calcination appeared as course light yellow powder (Figure 1a), in contrary to the white powder reported previously. The powder viewed under ultraviolet light glowed orange as illustrated in Figure 1b. The colour variation may be attributed to the extraneous component from the neem extract mixed with the zinc oxide powder, as they may vary from species to species.

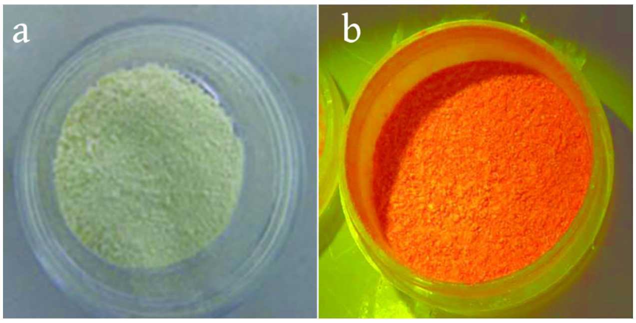

Figure 1: Nanostructured zinc oxide powder viewed under a) white light and b) ultraviolet light. Although zinc oxide powder exhibited slight photoluminescence, the intensity was not strong.

Figure 2 represents the micrograph of the fabricated nanostructured zinc oxide powder exhibiting highly agglomerated particle forming intricate nanostructures. EDS results of the nanostructured zinc oxide powder elemental study illustrated in Figure 3 showed the presence of a small amount of impurities, originating from the neem extract. Otherwise, it showed a weight percentage of 75 % zinc and 23 % oxygen atoms. IR spectra of Neem extract (Figure 4) shows bands

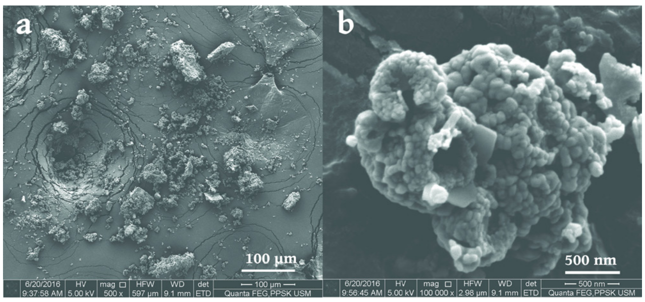

Figure 2: High-resolution micrographs of nanostructured zinc oxide captured under varied magnifications a) 500x and b) 100 000x. The micrographs revealed highly agglomerated nano-sized spherical zinc oxide particle forming micron sized structures. Lower magnification images clearly showed presence of clumped particle and minimal dispersal.

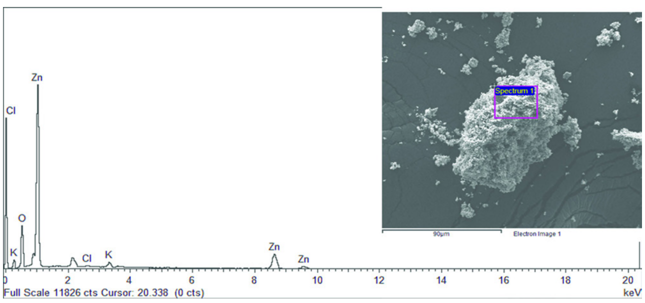

Figure 3: EDS spectra of nanostructure zinc oxide. Elemental analysis conforms to the presence of zinc and oxygen elements as well as some metallic impurities that can be attributed to the neem extract residue.

characteristic of terpenoids and other antioxidants. O-H (broad stretch along 3400 cm-1) stretch band was observed along with C=O peak (1384 cm-1) shows the presence of aliphatic carboxylic acid. C-F peak at 1105 cm-1 corresponds to mono and polyfluorinated compounds. Absorption bands 1633 and 1271 cm-1 corresponds to the presence of aromatic rings and saturated primary alcohol respectively. There was a prominent doublet absorption present at 2921 cm-1 in the Neem extract and nanostructured zinc oxide powder is a classic characteristic of aromatic aldehyde indicative of terpenoids group. A clear plunging absorption band was observed in nanostructured zinc oxide powder IR spectra at 441 cm-1 characteristic of nanostructured zinc oxide. The yield of nanostructured zinc oxide powder was approximately 13 to 18% for every 2 grams of zinc nitrate utilised.

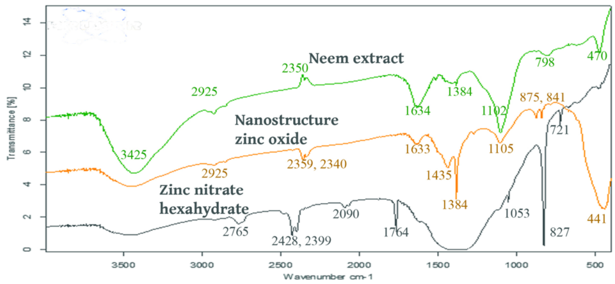

Figure 4: FTIR spectra of neem extract, nanostructured zinc oxide and zinc nitrate hexahydrate. Analysis indicated the conversion of zinc nitrate into nanostructured zinc oxide with a characteristic peak at 441 cm^{-1}.

Fabricated nanostructured zinc oxide powder was applied on latent fingermark and the image developed was studied under SEM to determine the powder's selectivity and distribution. Direct view of the fingermark developed showed sufficient contrast on a dark background and revealed characteristic ridge details as compared to when viewed under ultraviolet light, which diminished the contrast (Figures 5a and b). In contrast, the SIRCHIE white powder exhibited higher background interaction as can be observed as the ring of halo around the ridges (Figure 5c). The fingermark possessed good clarity, whereby minimal powder adherence to the spaces in between ridge was observed (Figure 6a). Nevertheless, clumping of the powder discouraged the homogenous distribution of the particles along the ridge reducing the quality of ridge border demarcation. In comparison, the SIRCHIE powder particles are heavily distributed on the ridges forming poor ridge demarcation lines (Figure 6b).

DISCUSSION

The various phytochemicals and enzymes content of the Neem extract facilitates the oxidation or reduction of the metal compound into the nanoparticle. Neem extract contains a high amount of terpenoids, which have been postulated to be the main reduction and stabilising

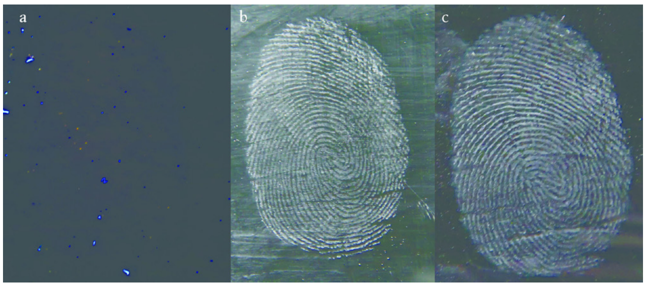

Figure 5: Latent fingermark developed using nanostructured zinc oxide powder viewed under a) ultraviolet light, b) white light and c) latent fingermark developed using SIRCHIE white powder viewed under white light. Clear fingermark ridge details were visualised after developed allowing the identification of primary, secondary and tertiary level of fingermark details, in contrast to the conventional SIRCHIE powder. The conventional powder exhibited a halo like appearance around the ridges indicating high background interaction. However, the luminescence of the zinc oxide fingermark under ultraviolet light was weak and did not provide sufficient contrast for detailed analysis.

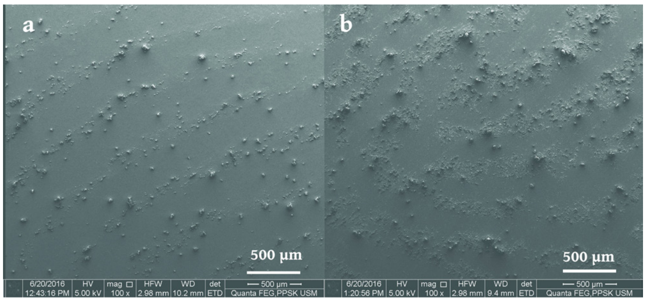

Figure 6: High-resolution micrographs of latent fingermark development using a) nanostructured zinc oxide powder and b) SIRCHIE white powder. The powder particles can be observed to be distributed selectively on the fingermark ridge residue, nonetheless the particles are not homogenously distributed along the surface, hence reducing quality of ridge definition. The SIRCHIE white powder particles are heavily distributed on the ridges forming poor ridge demarcation lines.

agent in the formation of nanostructured zinc oxides (8). Another report highlighted the production of zinc oxide nanoparticle using neem leaves extract, sodium hydroxide and zinc acetate as the precursors. They reported the production of 9 to 25 nm mono-dispersed spherical particles in liquid form. Comparative studies using varied plant extract showed that the shape of the particles formed was influenced by the extract employed (8,19). Present findings concur with these findings, whereby spherical particle was observed in the nanostructure of the zinc oxides. Nevertheless, the agglomeration may be particularly enhanced in the solid state as observed in our discoveries.

The fingermarks developed using the organically synthesised nanostructured zinc oxide powder exhibited good clarity and contrast on dark non-porous surfaces. The particle adherence seems to work based on mechanical factors alone specifically the attraction of the particles to the greasy counter-part of the fingermark residue. A high degree of particle aggregation led to the formation of unevenly layered particles on the fingermark ridges. In contrast, the SIRCHIE white powder has an affinity for both fingermark residue and substrate reducing the contrast of the ridges. Nevertheless, the zinc oxide powder possessed no significant luminescence under the ultraviolet light source.

Previously application of zinc oxide nanoparticle synthesised using the conventional synthetic precursor have also been applied for fingermark development. Authors reported the synthesis of flower-like structures in the dimensions of one to three microns applied as a wet particle suspension on non-porous surfaces. Excellent contrast and ridge detail visibility was reported in this study (1). Otherwise, the use of zinc oxide as a secondary suspension in the multimetal deposition technique have also been reported. Findings of this research indicated enhancement in contrast in comparison to the conventional multimetal deposition technique, however, authors stipulated that the contrast may be further enhanced by doping the zinc oxide particle with external photoluminescent particles similar to our reports (20).

Other metal oxides such as titanium dioxide, silicon dioxide and iron oxide have been exploited for the purpose of latent fingermark development (21–23). Nonetheless, the photoluminescent property of these metal oxide is not as strong as zinc oxide. Current synthesis technique exhibits slight luminescence dampening of the zinc oxide particle, which can be further enhanced by increasing the monodispersity of the particles and reducing the content of impurities.

CONCLUSION

This work reports a preliminary effort of utilising nanostructured zinc oxide particles fabricated through a green chemistry approach for the development of latent fingermarks. Future work may be conducted to enhance the structure of the particles to synthesised homogenously dispersed particles and confer strong luminescent to the powder. Nevertheless, this report lays a groundwork for the upcoming improvement of the powder characteristics and incorporation of green chemistry approach in the forensic field.

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