

# Synthesis of Carbon Nanoparticle from Rice Husk by Acid Digestion for Fingerprint Dusting Application

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## Abstract

Fluorescent carbon nanoparticle (CNP) was synthesised using acid digestion and thermal ageing of rice husk. The structural and chemical composition of CNP formed was studied using various analytical techniques, including FTIR, FESEM, HRTEM, EDS, XRD and surface area analyser. Acid digestion of rice husk followed by the thermal ageing of filtrate resulted in the formation of a black colloidal solution containing CNP with a distorted spherical shape in the range of 100 to 600 nm with a mean particle size of 385 nm. Chemical composition of CNP was confirmed by EDS and FTIR analysis and the amorphous nature of CNP was determined using XRD. FESEM and TEM analysis revealed slightly irregular spherical particles with a high degree of agglomeration. Freeze-drying produced mesoporous pore volume (0.009 cm<sup>3</sup>/g) CNP powder with an average pore size of 61.75 nm (0.89 to 81.90 nm pore size distribution) and low specific surface (0.558 m<sup>2</sup>/g BET and 4.816 m<sup>2</sup>/g BJH). CNP powder allowed the development of latent fingerprint of high clarity and clear ridge details.

**Keywords:** carbon nanoparticle, powder dusting, rice husk, fluorescent

## Introduction

Copious research has been devoted to produce nanomaterials due to their malleable size-dependant properties whilst their bulk counterpart exhibits fixed properties [1]. Efforts to synthesise various novel nanomaterials are still ongoing regardless of the abundant discoveries mainly to improve physical properties and chemical functionality of the nanomaterials to diversify its uses. There are also needs to discover not only new nanomaterials that are sustainable, non-toxic, biocompatible and environmentally friendly but also to adopt a green synthesis process using renewable precursors.

CNP has demonstrated to be a viable alternative to quantum dots due to inane advantages such as bright fluorescence, high photostability as well as tunable excitation and emission spectra. CNP also exhibits less toxicity, soluble in water, chemical inertness and has good biocompatibility as have been reported. Intrinsic properties of CNP can be finely tuned by altering the morphological and structural parameters leading to various research in synthesising micro and nanospheres of carbon [2,3]. CNP nanospheres can be categorised into three groups based on the size of the pores, namely micropores (<2nm), mesoporous (2-50 nm) and macropores (>50 nm) [4].

Energy shortage and environmental crisis has been an ever growing concern, requiring a facile, low cost, sustainable, environmentally non-toxic routes

of CNP production that can sufficiently meet customer demands [5]. In this instance, biomass appears as an excellent alternative precursor offering high quality and readily available ingredients to meet the demands [6]. Numerous research has utilised natural resources such as glucose, sucrose, citric acid, pomelo peel, willow bark, oatmeal, rice husk and honey to produce CNP [1,7–10]. In this paper, a method to synthesise CNP powder from rice husk (RH) using simple acid digestion was proposed, aiming to apply for fingerprint development.

## Experimental details

### Materials

RH was obtained from the local rice mill Bernas in Peringat, Kelantan, Malaysia. Hydrochloric acid (HCl, 37%) and ethanol puriss were purchased from Merck Millipore (Darmstadt, Germany). HI-FI Volcano Latent Print Heavy Black (No.HLP01) were purchased from SIRCHIE Youngsville, NC and used without modification.

### CNP synthesis

RH was cleaned and dried in hot air oven at 100°C overnight. Dried RH was grounded into fine particles using a regular counter top blender. Blended RH was refluxed in a solution of 1 M HCl at the ratio of 15 g RH to 500 mL acid. Acid treatment was conducted for an hour under vigorous magnetic stirring and constant

temperature at 80°C. The mixture was then filtered, leaving a dark orange filtrate. The volume of the filtrate was adjusted to 300 mL using deionised water. The solution was split into two separate flasks and kept in oven at 90°C for 12 hours. Experiment was repeated with different ageing periods of 15, 18 and 48 hours. Powders obtained at ageing intervals were named CNP<sub>12</sub>, CNP<sub>15</sub>, CNP<sub>18</sub> and CNP<sub>48</sub>, respectively.

The black colloidal solution formed was transferred into 50 mL eppendorf tubes and centrifuged at 5000 rpm for 15 minutes. The supernatant was discarded and the precipitate was washed thrice with hot deionised water to remove all traces of acid. The precipitate was dried in an oven at 80°C by alcohol dehydration. 5 mL ethanol was added to precipitate and the solution transferred into a crucible for drying.

### Characterisation of CNP

Characterisation studies of the powder were carried out to determine the physical and chemical characteristics of the CNP using Field emission scanning electron microscopy (FESEM: Quanta FEG 450 manufactured by the FEI Czech Republic), energy dispersive x-ray spectroscopy (EDX: Xmax 50mm<sup>2</sup>, Oxford, United Kingdom), High-resolution transmission electron microscopy (HRTEM: FEI Tecnai G2 High-Resolution TEM by FEI Czech Republic), surface area analyser (Autosorb 1, Quantachrome Instruments, Florida, USA), Fourier transform infrared spectroscopy (FTIR: Tensor 27 FTIR spectrometer by Bruker Corporations, UK), x-ray diffraction analysis (XRD: D8 Advance X-ray Diffractometer, Bruker Corporations, UK) and ultraviolet-visible

spectrophotometry (UVS: Varian Cary 100 Bio UVS, Varian, Australia Ptd. Ltd.).

### Application of the CNP powder to develop latent fingerprint on non-porous surface

CNP powders from different ageing period were collected and applied onto fingerprint using squirrel hair brush. Natural fingerprints were firstly deposited on a non porous surface and left at room temperature for an hour prior to the application of the powder. The fingerprints developed were evaluated based on the clarity of the ridges and the contrast between the fingerprint and the substrate.

### Results and Discussion

The yellow filtrate after the acid digestion of RH appeared as brown to black colloids after ageing. Precipitates of various shades of brown were produced upon high-speed phase separation.

In this study, CNP powder synthesised at different ageing time had different shades of brown, in which finest powder was relatively lighter in colour. Fingerprints developed using CNP<sub>12</sub> and CNP<sub>15</sub> had poor contrast and clarity (Figures 1a and 1b). By comparison, fingerprint developed using CNP<sub>18</sub> offered better contrast and clarity (Figure 1c). Ridges were well formed and clear demarcation was observed between fingerprint grooves and valleys in addition to substantial contrast between surface and ridges. On the other hand, CNP<sub>48</sub> exhibited very poor adherence to fingerprint residue (Figure 1d). Hence, CNP<sub>18</sub> was further studied to determine its physicochemical characteristics.

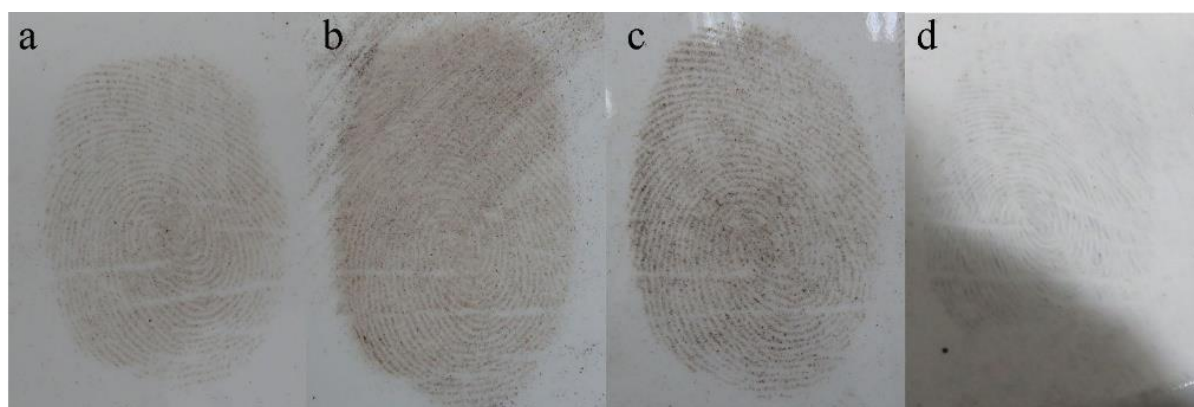


Figure 1: Fingerprints developed with a) CNP<sub>12</sub> b) CNP<sub>15</sub> c) CNP<sub>18</sub> d) CNP<sub>24</sub>

SEM micrograph of fingerprint developed using CNP<sub>18</sub> (Figure 2) revealed clear ridge details with minimal interaction of the powder particles with the substrate bearing the fingerprint. Rounded and nanosized CNP<sub>18</sub> particle promoted good adhesion

selective to fingerprint ridges. Results indicated that CNP<sub>18</sub> powder possessed selectivity and sensitivity for fingerprint residue which were characteristics of good quality fingerprint developing powder.

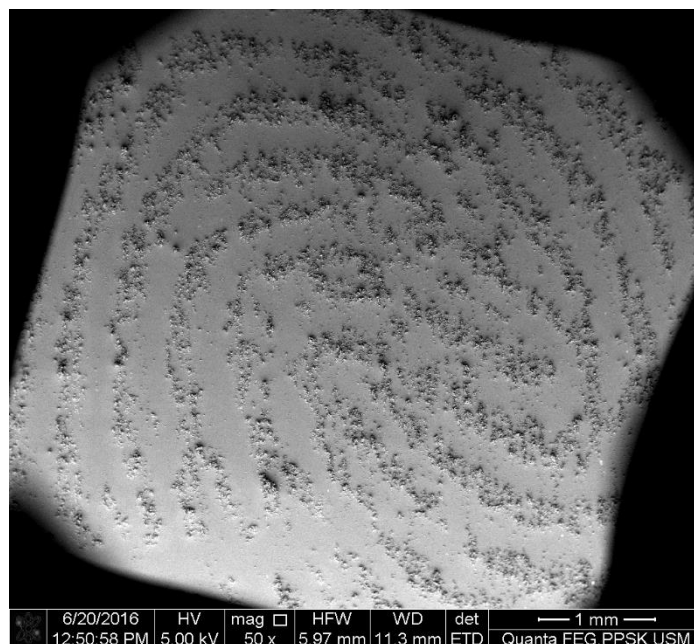


Figure 2: SEM micrograph of fingerprint developed using CNP<sub>18</sub> powder

Figures 3 and 4 demonstrate the results of the characterisation studies conducted on CNP<sub>18</sub>. Figures 3a and 3b show representative TEM micrographs of the CNP<sub>18</sub> revealing spherical particles with a certain degree of agglomeration. A typical XRD pattern (Figure 3c) expressed a broad diffraction peak from 10° to 30° centred at approximately 15° and 22°, indicating the amorphous nature of the CNP<sub>18</sub> powder.

UV-visible absorption study was conducted on CNP<sub>12</sub>, CNP<sub>15</sub> and CNP<sub>18</sub> powders (Figure 3d). CNP<sub>48</sub> was not water soluble and therefore omitted in this experiment. CNP powders produced from different ageing intervals exhibited slight shift in maximum absorption. Absorption was recorded at 276 nm and 235 nm, 310 nm and 227 nm as well as 281 nm and 211 nm for CNP<sub>12</sub>, CNP<sub>15</sub> and CNP<sub>18</sub>, respectively. The absorption peak shift could be attributed to the change in particle size with the lightest colour intensity produced by smaller particle size.

SEM micrographs (Figures 4a-b) revealed slightly irregular spherical CNP particles with a high degree of agglomeration and large pores. Particle size analysis was conducted using the SEM images using Image J software, and the representative histogram was generated using IBM SPSS software

(Figure 4c). The particle size distribution fell in the range of 100 nm to 600 nm, with a mean particle size of 385 nm, as depicted in the histogram.

The chemical composition of powder was confirmed by EDX (Figure 4d), showing the presence of carbon and oxygen atom at an atomic ratio of 7 to 3. The oxygen atom could be originated from the zinc oxide suspension used to place the specimen. The results has suggested high purity of CNP powder [11].

IR spectra of CNP<sub>18</sub> powder (Figure 4e) was acquired to determine the surface functional groups, demonstrating peaks characteristic of C-OH, C-H and C=O at 3420, 2934 and 1613 cm<sup>-1</sup>, respectively [12]. The sharp peak at 1513 cm<sup>-1</sup> was ascribed to N-O bond and symmetric/asymmetric vibrations of carboxylates groups were identified at 1384 and 1265 cm<sup>-1</sup> [13]. Bands in the range of 1000 – 1450 cm<sup>-1</sup> could be attributed to C-O stretching and O-H bending vibrations, implying the existence of residual hydroxyl groups. The band at 830 cm<sup>-1</sup> corresponds to C-H out of plane bending vibrations [6]. All the IR analysis results indicated that the surface of CNP was rich with hydrophilic group consistent with previous reports [12,14]. These functional groups were originated from the breakdown of lignocellulose in RH.

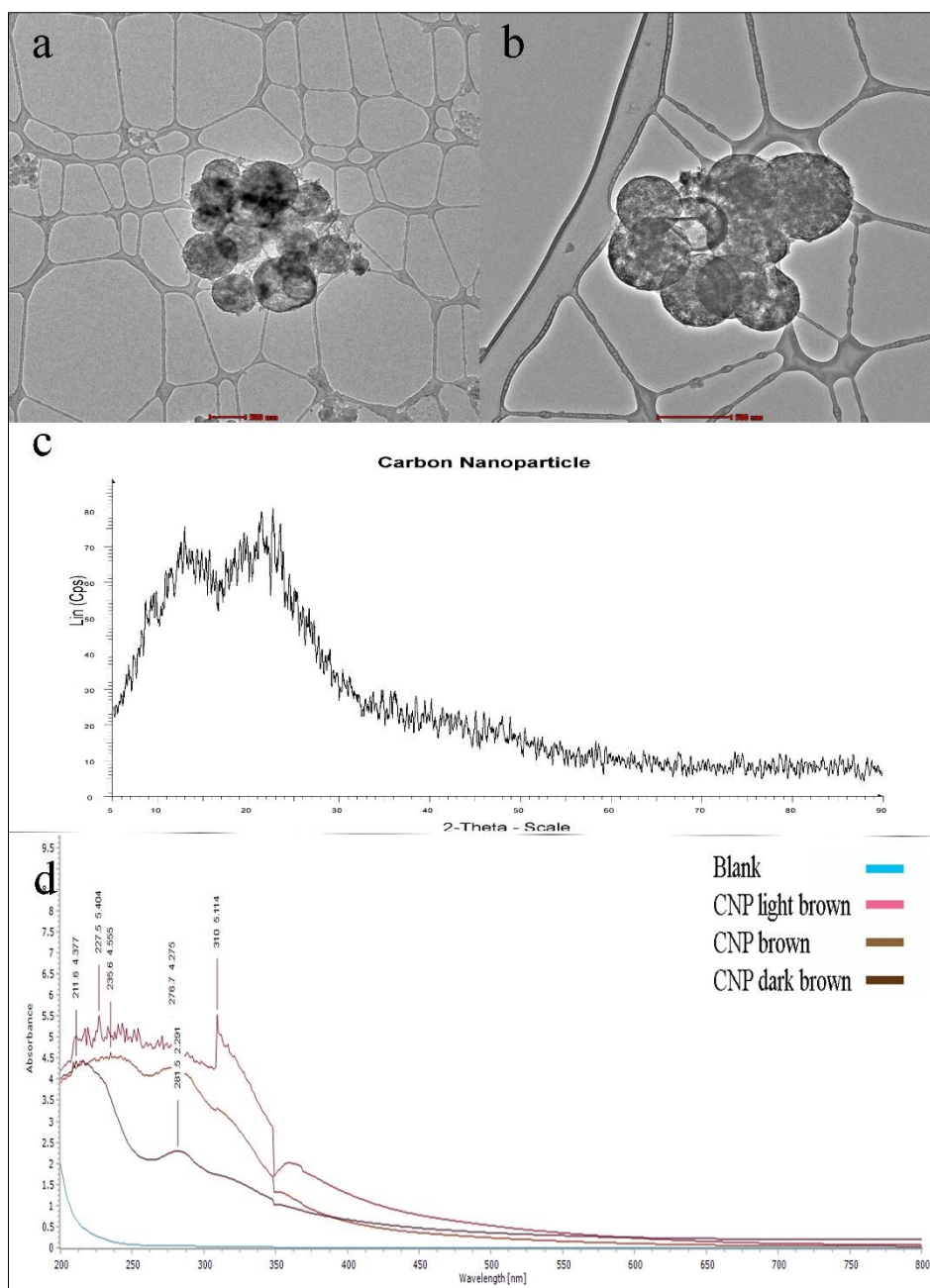


Figure 3: a-b) TEM images of CNP c) XRD spectrum d) UV-Vis absorption spectra of CNP<sub>12</sub>, CNP<sub>15</sub> and CNP<sub>18</sub>

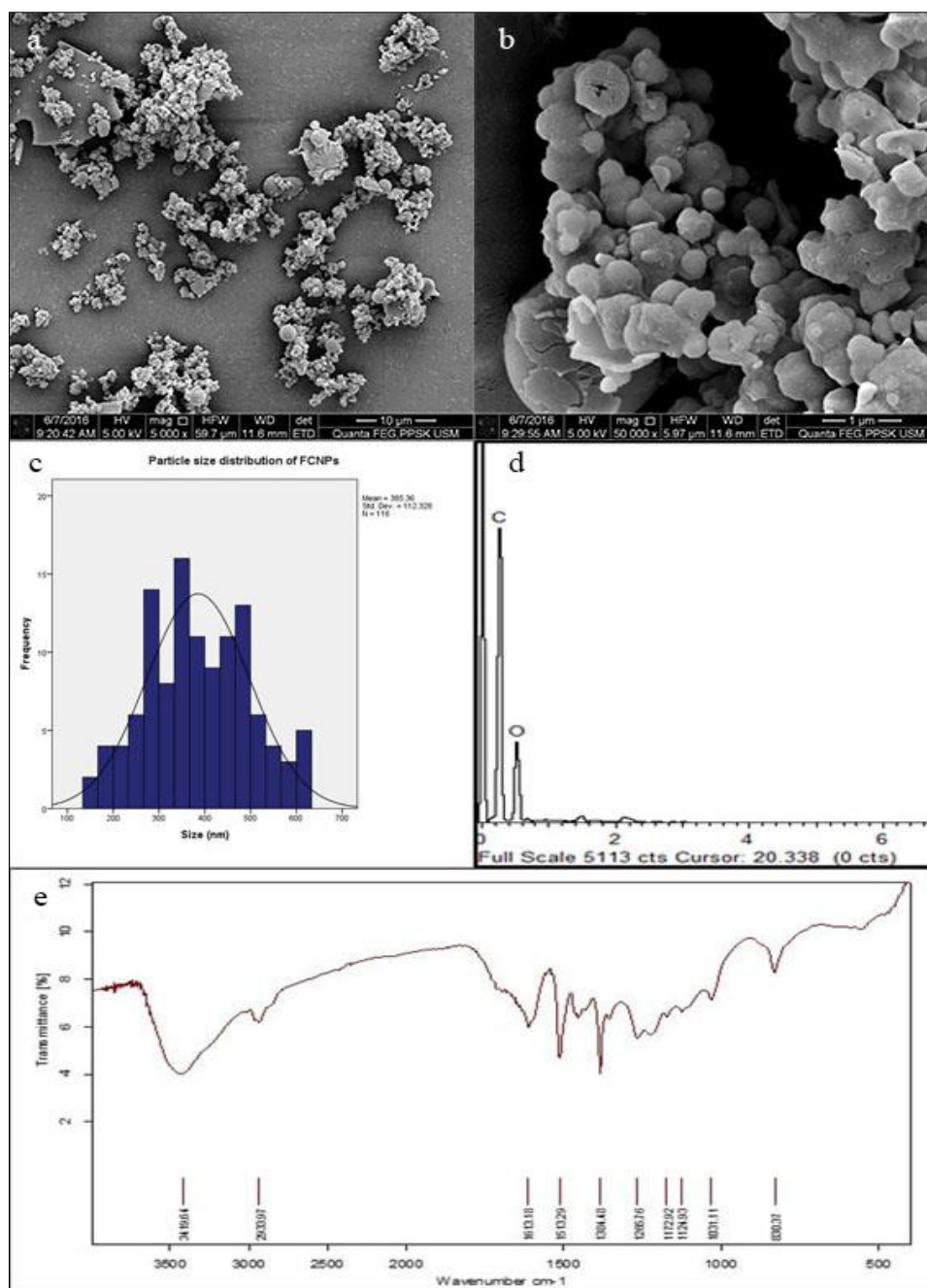


Figure 4: a-b) SEM images of CNP b) histogram particle size distribution of CNPs showing mean particle size of 385 nm c) EDS spectrum d) FTIR spectrum

In this study, the fluorescent CNP was found with excellent water dispersibility without any ultrasonic assistance except CNP<sub>48</sub>. Colloidal solution after ageing also exhibited a bright blue-green fluorescence characteristic under UV light even at very dilute concentration. The fluorescence was strong enough to be viewed without any optical assistance. However, the phenomenon was not observed when CNP powder was dispersed in water. This is presumably because the fluorescent CNP were water soluble and could not be separated by centrifugation. The precipitated powders were larger particles with no fluorescent property.

Water soluble fluorescent CNP can be extracted by neutralising the aqueous solution obtained after phase separation. These particles can be an excellent alternative for quantum dots in applications such as bio-imaging studies because of its photo stability, chemical inertness and low toxicity [15–17]. CNP<sub>48</sub> can be used to develop colour pigments in paint and cosmetic industries [18].

Nitrogen adsorption-desorption isotherm was determined to be Type IV isotherm with a type H3

loop according to the IUPAC classification, indicating a mesoporous structure [7]. Pore size distribution analysis performed by the BJH method determined that CNP possessed pore size distribution ranging from 0.89 to 81.90 nm with an average pore width of 61.75 nm.

The BET surface area of CNP powder was 0.558 m<sup>2</sup>/g and the BJH cumulative surface area was 4.816 m<sup>2</sup>/g. The relatively higher surface area calculated by the BJH method in comparison to BET analysis points toward a porous material. However, the low surface area in comparison to previous reports indicated large cluster of particles and pore size. The total pore volume of CNP powder from RH in this study was reported at 0.009 cm<sup>3</sup>/g, much lower than previous studies with approximately 1.300 cm<sup>3</sup>/g [6,7]. The yield percentage of CNP powder in this study was determined in the range of 5.4 to 7.2%.

### Conclusion

Pure CNP powder was synthesised using acid digestion of RH and subsequent thermal ageing of the filtrate. Lignocellulose present in the RH was leached out to into the acid solution and ageing of the filtrate in oven resulted in black colloidal solution containing CNP. The method is simple, environmentally friendly and does not require high temperature during synthesis. CNP powder synthesised in this study was a by-product of silica nanoparticle extraction from RH. CNP<sub>18</sub> was found to exhibit superior performance in comparison to other CNPs, and therefore selected due to the good clarity and contrast of the ridges developed. Limitation of this technique arises from the use of corrosive acid for the synthesis of CNP from RH. Further research using another medium such as ionic liquids or a different technique such as microwave-assisted thermal digestion to produce CNP from RH is to be explored.

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