FACILE SYNTHESIS OF CNT COTTON/ZnO NANOCOMPOSITE USING WASTE COOKING OIL AS THE BIOTEMPLATE VIA HYDROTHERMAL/CALCINATION PROCESS

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Abstract. One of the common domestic wastes that are abundantly available is waste cooking oil (WCO) where improper disposal will create problems such as clogging the drain and/or related sewage system. Whether this carbon-rich waste can be up-converted for the formation of CNT and/or as a biotemplating agent for the formation of ZnO-CNT nanocomposite is the subject of interest of this research work. Therefore, the focal point of this work is to use this carbon-rich waste material, WCO as a biotemplate of ZnO growth onto the surface of carbon nanotube cotton (CNTC) for the formation of CNTC/ZnO nanocomposite. The results from the physicochemical analyses showed that WCO plays a dual role; as a carbon precursor for the formation of CNTC and as a templating agent to grow ZnO in the preparation of CNTC/ZnO nanocomposite. In the latter, the WCO was attached to the surface of CNTC and acted as the nucleation site for the ZnO growth which then formed the CNTC/ZnO nanocomposite, as indicated by the presence of the COO-Zn bond in their FTIR spectra. XRD studies showed the presence of the carbon, ZnO and iron oxide phases, confirming that the resulting nanocomposite is composed of CNTC and ZnO as the main components, while the presence of iron oxide is due to the catalysts that were used for the synthesis of the CNTC. The degradation of the sp^2 graphitic phase was observed in the Raman spectra, indicating the defects of sp^3 became prominent, due to the formation of the COO-Zn bond.

Keywords: CNT, waste cooking oil, biotemplate, ZnO, palm oil, green

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Introduction

Carbon is an element that is available in abundance and has many allotropes. Examples of carbon allotropes are amorphous carbon, graphite, activated carbon, carbon nanotubes, diamond and fullerenes. Recently, graphene which was exfoliated from layers of graphite was discovered. The latest discovery reported that the fragment of graphene is known as graphene quantum dots which have interesting photoluminescence properties. Nowadays plethora of carbon sources are used to synthesize various types of carbon allotropes; coal, graphite, CO2 gas, petroleum derivative products, etc. Previous reports indicated that extensive works have been carried out to explore green, renewable carbon sources to synthesize various carbon nanomaterials. There are many types of green carbon-based sources subjected to research especially renewable resources such as palm oil, corn oil, glucose, husk rice, biomass, etc.

Recent reports have shown that palm oil-based cooking oil can be used as the carbon precursor to synthesize various types of carbon nanomaterials such as carbon nanotubes (CNT) [1-2], carbon spheres [3-4] carbon nanohorns [5], activated carbon [6-7], carbon nanotubes cotton [8], etc., as palm oil is carbon-rich material. Moreover, the work that used waste cooking oil as the carbon precursor to synthesize carbon nanomaterials also was highlighted [8-9]. This work is also beneficial to society as a kind of waste management, where WCO can be converted into useful carbon nanomaterials that find a wide range of applications.

By their chemical nature, most carbonaceous nanomaterials are hydrophobic. This is due to its pure aromatic carbon layers which caused them to be easily agglomerated, hindering the dispersion in aqueous, solvents or any polymer melts. However, their degree of hydrophobicity differs due to the availability of the moieties at the edges of different carbon nanomaterials. The degree of hydrophobicity can be decreased as these moieties are oxygenated which becomes more hydrophilic. Moreover, the diameter of the CNT and the temperature also played a role in the hydrophobic/hydrophilic characteristics [10]. Recent reports highlighted that the characteristic of CNT towards aqueous or any solvents can be tailor-made by the addition of liquid hydrocarbons and polycyclic aromatic hydrocarbons such as phenanthrene and naphthalene [11-12]. Other works also reported that introducing oxidation and alkalization would attach the hydroxyl and carboxyl groups and cause a few defects on the surface that could improve the hydrophilicity of the CNT [13].

With the large specific surface area of the CNT along with its hydrophobic/hydrophilic characteristics, extensive work has been done to use it for oil removal. The superlative absorption properties emphasize that CNT has become the ideal candidate to replace more traditional adsorbent materials such as activated carbon, organoclays, wool and zeolites. Previous works demonstrated and provided insight understanding on the potential of multiwalled CNT to adsorb hydrocarbon from water [14-15]. More importantly, the ability of CNT to adsorb oil with 123 times its weight was further highlighted [16]. Other works have also shown that CNT could adsorbed benzene which is composed of pure aromatic carbons [17].

Besides being exploited as the carbon precursor for carbon nanomaterials, palm oil has also shown to be a good biotemplate. Various shapes of ZnO particles such as flakes-, flower-, and three-dimensional, star-like structures were obtained using the hydrothermal method. It was shown that palm oil could be used as a shape modifier due to the interaction between the carboxyl group of palm oil and the zinc species of the precursor [18]. Similar work has shown the important role of rape pollen grains as a biotemplate, as the shape of the grain swayed the shape of the bilayer structure of microspheres [19]. Replicating titania-based solids according to the shapes of the biotemplate can be done using olive leaves for enhanced solar light harvesting applications [20].

ZnO, which is a semiconductor material is widely used in electronic applications. This is due to its large exciton binding energy of 60 meV, a direct band gap of 3.3 eV, near-ultraviolet emission, and piezoelectric. Various substrates were used for ZnO growth such as glass, indium tin oxide (ITO) and silicon. Another major application for this metal oxide is as an antibacterial. The use of ZnO has attracted a lot of research due to the development of antibiotic resistance against bacteria. Extensive reports have been well documented emphasizing the promising use of zinc oxide nanoparticles against gram-positive and gram-negative bacteria. Moreover, the antibacterial activity could be improved by reducing the ZnO particle's size and increasing the surface area, altering the surface properties and its interactions with cells. Previous studies also reported that ZnO is clinically used against Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, and Bacillus subtilis.

The literature reviewed above shows that CNT was more hydrophobic, therefore it is quite difficult to obtain a good distribution for zinc nucleation sites and attach them onto the CNT surface, simply by just soaking them in zinc acetate solution. An extra treatment is required such as introducing functional or alkenes groups to enhance its affinity towards the zinc acetate species from the solution. In addition, other work demonstrated the seeding technique using a zinc sputter coater is useful for impregnating ZnO seeds onto the CNTC.

In this work, the preparation of CNT/ZnO nanocomposite using hydrothermal and calcination processes was carried out. A green carbon precursor, waste cooking oil (WCO) was used as the biotemplate for the growth of ZnO particles onto the carbon nanotubes cotton. In addition, the CNTC also was synthesized using WCO as the carbon precursor. The main focus of this work was to use recycled WCO as a green, renewable carbon source for the production of CNTC and as a biotemplate agent for ZnO growth. Their physicochemical analyses were conducted to study the effect of various loading of WCO on the growth of ZnO particles on the CNTC for the formation of their nanocomposite.

Materials and Methods

Materials

Palm oil-based waste cooking oil (WCO) was obtained from a local restaurant. This WCO was used as the biotemplate and also as the carbon precursor for synthesizing the CNTC. The CNTC was produced in our laboratory. Zinc acetate hexahydrate (Sigma Aldrich; CAS 5970-45-6) without any purification was used in this work as the zinc precursor.

Preparation of CNT-Cotton

The same WCO was used for the preparation of the CNTC. It was first filtered to remove any solid contaminants and then heated at 100 °C for the removal of any volatile impurities and water. A horizontal tubular furnace for chemical vapor deposition of the CNTC was used in this work. A mixture of WCO, ferrocene, and thiophene was heated at 1150 °C under an argon flow to obtain the CNTC. The details of the work were fully described elsewhere [8].

Prepration of CNTC/ZnO Nanocomposites

The method of the preparation of the CNTC/ZnO nanocomposites is summarised in Figure 1. A zinc acetate solution of 0.1M was prepared in a 500 mL beaker. 2 grams of CNTC was added into 50 mL of 0.1 M zinc acetate solution and stirred for 30 minutes. Then various WCO mass was added into each solution of 0, 0.1, 0.5, 1 and 2 g (w/w) and vigorously stirred for 3 hours to get a purplish color solution. The WCO which consisted of zinc acetate was adsorbed onto CNTC surface at this stage. About 30 mL of solutions, prepared earlier were then transferred into a 50 mL Teflon autoclave. A hydrothermal process was carried out at 150 °C, overnight. Then the sample was dried and followed by calcination at 500 °C for 3 hours using a chemical vapor deposition furnace under a continuous supply of nitrogen gas. The resulting sample was cooled down to room temperature and stored in a sample bottle for further use and characterization.

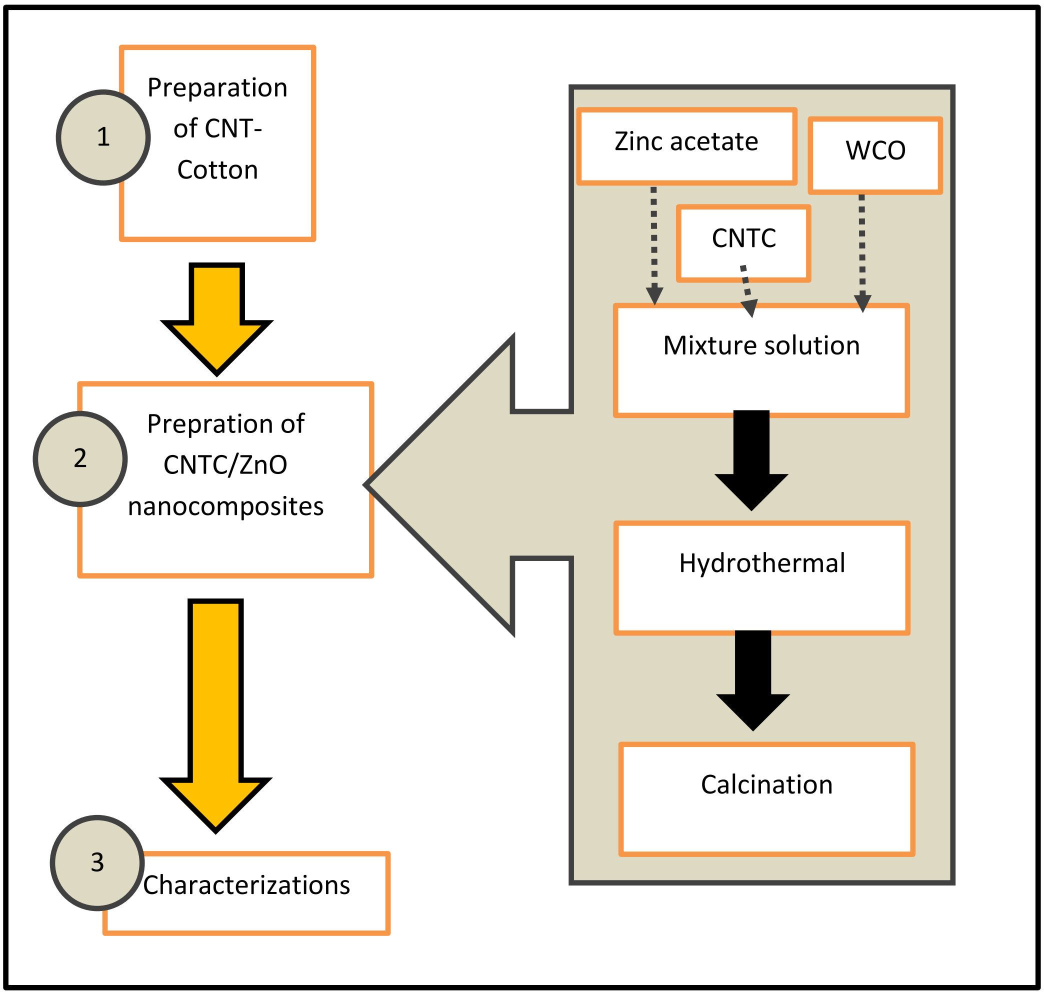

Figure 1: A flow chart of the method of the preparation of the CNTC/ZnO nanocomposites

Physicochemical Characterizations

a) X-ray Diffraction Analysis

CuKα radiation with a wavelength of 1.54 Å at 40 kV was used for the X-ray diffraction analysis (XRD). The XRD patterns of the carbonaceous materials were obtained at 2θ = 10 – 70° with an angle increment of 20° min^{-1} using an X-Ray diffractometer, Rigaku SmartLab X-ray diffractometer. The powder-formed samples were used for this characterization technique.

b) Morphological Images by FESEM

A field-emission scanning electron microscope (Zeiss, Supra 40VP) was used in this work. The dried sample was loaded on a stub and coated with gold using a sputter coater and transferred to the FESEM chamber for observation and analysis.

c) The Fourier-transform Infrared

The Fourier-transform Infrared (FTIR) spectra of the samples were obtained using a scanning wavenumber of 400 - 4000 cm^{-1} with a resolution of 4 cm^{-1}. (Vector 22, Brooke Spectrometer Company, Karlsruhe, Germany). The powder-formed samples were used for this characterization technique.

d) Raman Spectroscopy

Raman spectra were obtained using a Raman spectrometer, (DXR Raman microscopy, Thermo Fisher Scientific, Waltham, MA USA), equipped with a 532 nm Nd: YAG laser. The detection of the Raman scattered light was carried out using a Peltier-cooled InGaAs detector. For a Raman spectrum, the total laser exposure time was 2 seconds, and the laser power was set at 2.9 mW. The accuracy and precision of the acquired Raman bands spectra were less than 3 cm^{-1} and 1.5 cm^{-1}, respectively. The spectra of each sample were evaluated three times on the same day to assess the measurement reproducibility. The average Raman spectra of separate samples were used for comparisons and spectroscopic assessment. The powder form of the samples was used for this characterization technique.

e) Specific Surface Area

Nitrogen gas adsorption-desorption isotherm of the samples was recorded using a Micromeritics, Tristar II Plus instrument. The specific surface area of the nanocomposite was calculated using the BET equation. Both samples before and after the calcination process at 500 °C were subjected to this study.

Results and Discussion

a) Phase Analysis

The phases that are composed of the nanocomposite are of a crystalline material and were identified using the XRD technique. At the same, this technique allows the qualitative elemental analyses of the nanomaterials. The XRD patterns of the CNTC/ZnO nanocomposites synthesized using various amounts of WCO are shown in Figure 1. Sharp diffraction peaks observed in the XRD patterns indicated the highly crystalline nature of several phases that composed the nanocomposite; carbon, ZnO and iron oxide.

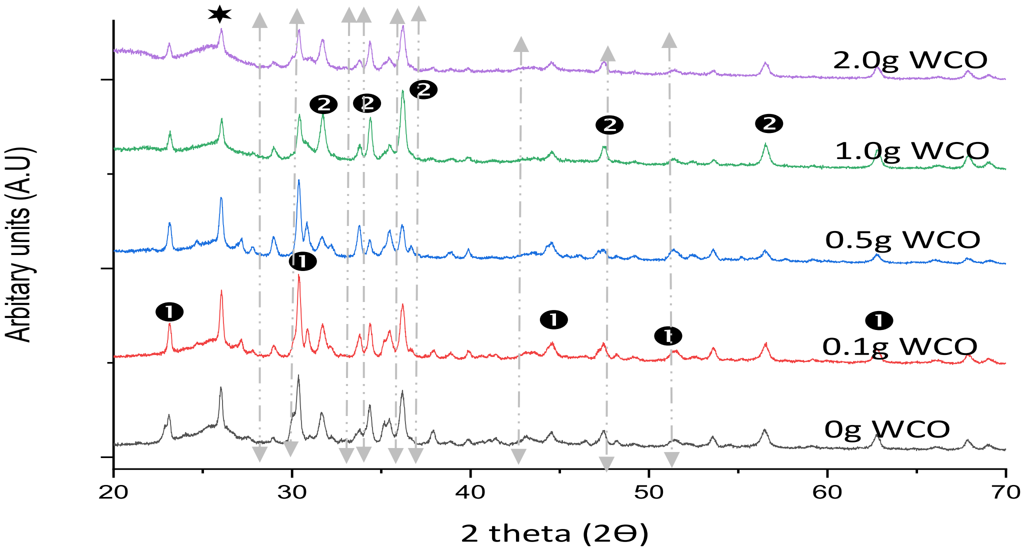

Figure 1: XRD patterns of CNTC/ZnO nanocomposite synthesized using various amounts of WCO (✶=graphitic carbon, ❶ = ZnO, ❷=iron oxide)

The graphitic phase of carbon, labelled by a (✶) was detected at 2θ = 26.5° corresponding to the (002) reflection (ICDD 41-1487) [2,29]. Several reflection peaks belonging to iron oxide are detected at 2θ = 22°, 30°, 35°, 44°, 52° and 63°, which correspond to the (102), (220), (311), (222), (400), (440) reflections (ICDD 39-1346) [30-32], respectively. The presence of an iron oxide phase in the nanocomposite (labelled by "❷") is due to the ferrocene which was used as the growth catalyst for the CNTC. The formation of the ZnO phase can be confirmed by the appearance of several reflection peaks at 2θ = 32°, 34°, 37°, 48°, and 57°. These reflection peaks are due to the (100), (002), (101), (102), and (110), respectively (ICDD 98-002-9272) [18,33].

Based on the XRD patterns, the nanocomposite is composed of two major phases; graphitic carbon of the CNTC and the ZnO nanoparticles which were biotemplated on the CNTC. The presence of the iron oxide phase is due to the oxidized catalyst that was used for the formation of the CNTC.

b) Morphological Study

The effect of the biotemplate on the formation of CNTC/ZnO could be clearly seen in the FESEM morphological images. The morphological images of the CNTCW/ZnO nanocomposites are shown in Figure 2. Formation of ZnO nanoparticles was clearly seen in Figure 2(a) and (b) and the appearance of a few CNT in between the ZnO nanoparticles at the inner side of the nanocomposite is observed with a diameter ranging from 60-130 nm.

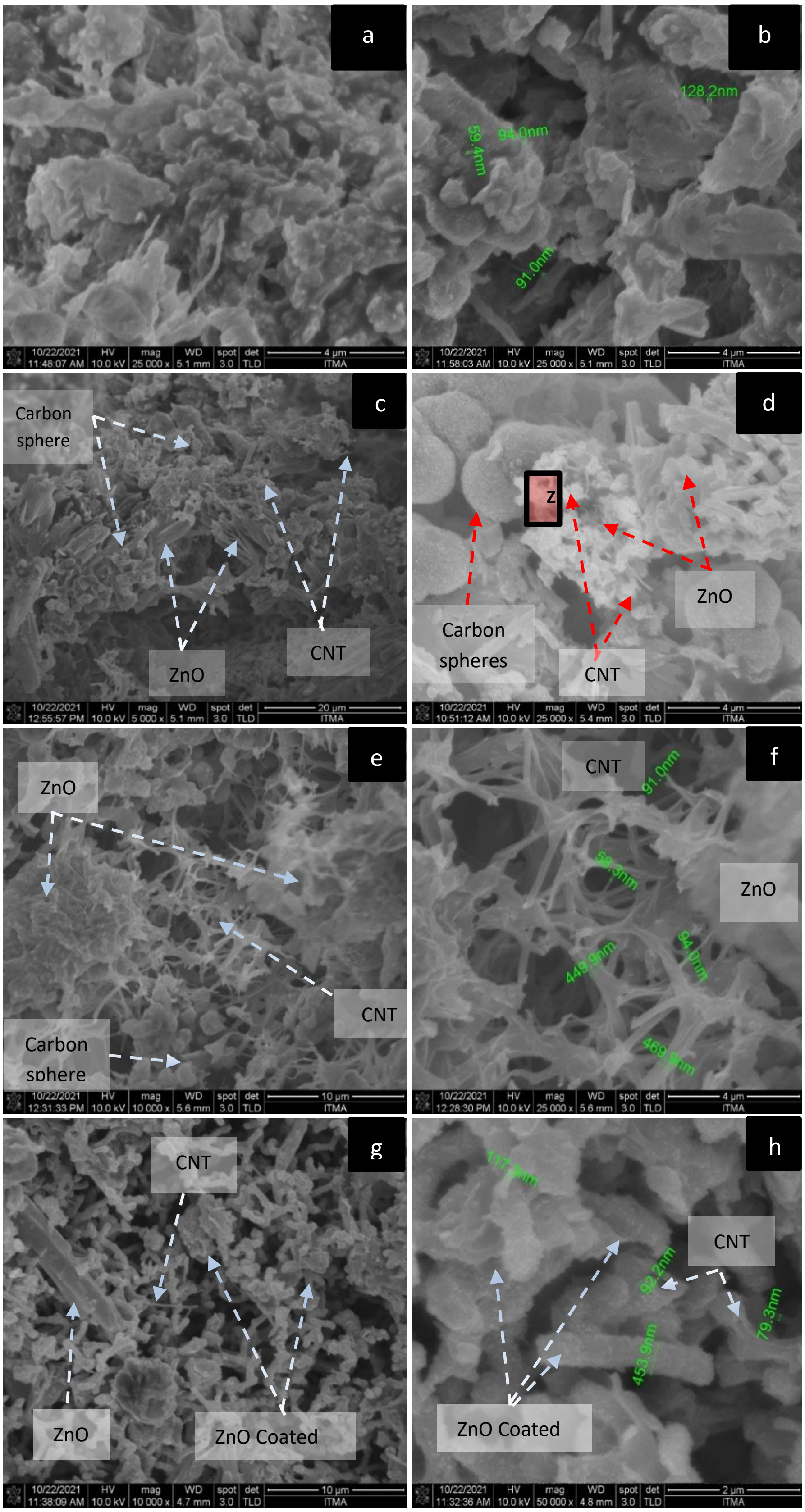

Figure 2: FESEM images of the CNTC/ZnO nanocomposites synthesized using various masses of 0 g WCO (a and b), 0.5g WCO (c and d), 1 g WCO (e and f) and 2 g WCO (g and h) taken at various magnifications

The morphological observations revealed that the hydrothermal treatment followed by the calcination process of a mixture of CNTC with zinc acetate solution resulted in the formation of ZnO nanoparticles onto the top surface of the CNTC. This is due to the hydrophobic nature of CNTC toward the zinc acetate solution.

However, the introduction of 0.5 g of WCO as the biotemplate, resulted in the formation of carbon-microsphere [3], ZnO and CNTC/ZnO nanocomposite as shown in Figure 2(c) and (d). Interestingly, it was found that the formation of carbon microspheres was also formed between the gap of the inner side of the nanocomposite. This piece of evidence showed that the oil-philicity nature of the CNTC could absorb the WCO, which also contained zinc acetate moieties during the hydrothermal treatment. WCO which acted as the biotemplate on CNTC and provided a nucleation site for ZnO [18]. The reaction between the carboxylic acid functional groups of the WCO and zinc acetate on the surface of the CNTC resulted in a conglomeration of ZnO particles as shown by the arrow 'Z' (Figure 2(d)). These images also indicated that the biotemplate acted as a shape modifier of ZnO at low concentrations of WCO [19-20]. The co-formation of the carbon microspheres in the nanocomposite is due to the WCO that is adsorbed on the surface of CNTC but without the presence of zinc acetate for the growth of the ZnO nucleation sites. Similar images were seen as more WCO content was added to the system as shown in Figure 2(e) and (f). The formation of microspheres and ZnO entangled between the CNTC also was observed. The difference was that several CNT diameters significantly increased to ~450 nm. Figure 2(g) and (h) shows the morphological images of the addition of 2 g WCO for the synthesis of the nanocomposite. ZnO rods were also observed (Figure 2(g)) however, the carbon microspheres disappeared as the WCO content was increased to 2 g. More importantly, bigger diameters of ZnO-coated CNT were observed (~450 nm) with good uniformity. At high magnification, the images revealed that the addition of the biotemplate could fully coat the CNTC with good uniformity as shown in Figure 2(h). This shows that the biotemplate could be used as the shape directing agent on the substrate, CNTC for the formation of the ZnO using hydrothermal and calcination processes [21].

The mechanism of "biotemplate" can be either described by replicating the morphological characteristics and the functionality of a biological species or by using a biological structure to guide the assembly of inorganic materials. WCO used in this work is palm olein (PO)-based cooking oil, composed of complex biomacromolecules of fatty acids of various chain lengths, carotenes, etc. Therefore, the biologically guided assembly of zinc nanostructures on the surface of CNTC has possibly occurred with the presence of PO functional groups. These functional groups are produced due to the hydrolysis of palm olein in water under our experimental condition, creating nucleation sites for zinc crystal growth and promoting the pattern or certain morphologies formation. The self-assembly is guided by the presence of the biotemplate and is directed by covalent or non-covalent interactions or molecular recognition processes. The electrostatic interaction may occur between carboxyl and hydroxyl groups of PO and zinc cations. This electrostatic attraction may also occur between primary and secondary particles resulting in the formation of complex structures. This is a soft-templating method because PO, an organic template, was used to synthesize the zinc oxide nanostructures.

The formation of the ZnO nanostructures consists of three steps; the self-assembly of the palm olein, the organization of zinc acetate over the PO self-assembly in a regular ordered array to form a stable inorganic-organic hybrid and finally, the successful removal of organic template to obtain the zinc oxide nanoparticles on the CNTC for the formation of the CNTC-ZnO nanocomposite.

c) Fourier Infra-red Spectroscopy

Figure 3 portrays the FTIR spectra for ZnO, CNTCW/ZnO nanocomposites without and with the addition of WCO at various loading amounts. Several bands are recorded at 839 and 1413, 1540, and 1651 cm^{-1}, corresponding to the formation of tetrahedral coordination of Zn and stretching vibration of the Zn-O bond.

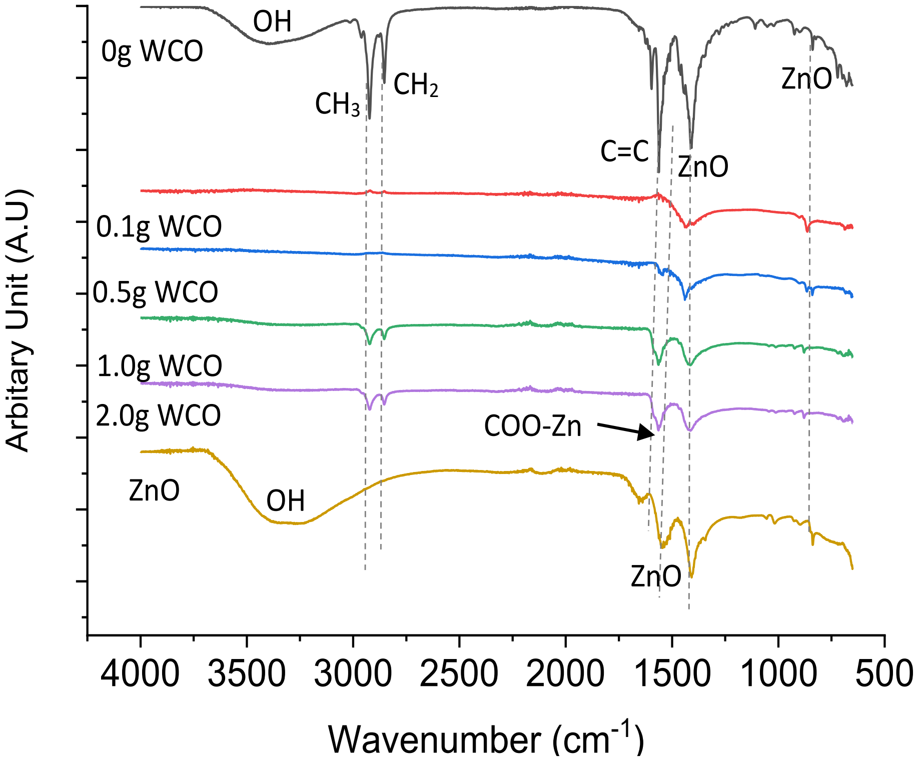

Figure 3: FTIR spectra of the CNTC/ZnO nanocomposites synthesized at various WCO contents; 0.0, 0.5, 1.0 and 2.0 g (w/w)

Another broadband at 3400 cm^{-1} is attributed to the O-H bending vibration. Few sharp bands are observed for the CNTC/ZnO nanocomposite. Both bands at 1411 and 1599 cm^{-1} were attributed to the stretching vibration of Zn-O. The appearance of a band at 1560 cm^{-1} was due to the C=C bond of CNT. Other CH_2 and CH_3 stretching vibrations of CNT were identified at 2850 and 2925 cm^{-1}, respectively. The addition of a small amount of WCO could significantly alter the chemical properties of the nanocomposite, as the C=C bond at 1560 cm^{-1} was shifted to a lower wavenumber at 1545 cm^{-1} which corresponds to the COO-Zn [18]. The presence of COO-Zn vibration indicated that the WCO acted as the biotemplate, attached to the CNTC surface which provides nucleation sites for the ZnO growth. The ZnO was well developed when the calcination process took place at 500 °C.

d) Raman Spectroscopy

Raman spectra for the CNTC/ZnO nanocomposite synthesized using various concentrations of WCO as the biotemplate agent is shown in Figure 4. The D and G bands can be located at 1350-1380 cm^{-1} and 1550-1600 cm^{-1}, respectively and are associated with the defects of the sp^3 and also the graphitic nature of sp^2, respectively [2,5].

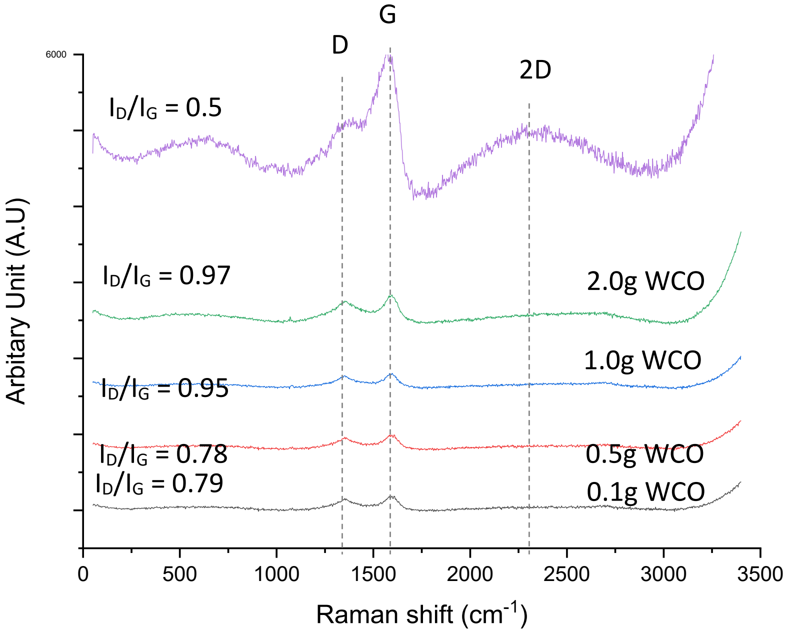

Figure 4: Raman spectra of the CNTC/ZnO nanocomposites synthesized at various WCO contents; 0.0, 0.5, 1.0 and 2.0 g (w/w)

The crystallinity degree of the graphitic nature can be estimated by the ratio of the I_D/I_G. It was found that the I_D/I_G value of the nanocomposite synthesized without WCOs was 0.5. The addition of WCO from 0.1 g to 2 g, used as the biotemplate resulted in the I_D/I_G value increased to 0.97. This information indicates that more defects were introduced in the CNTC/ZnO nanocomposite when a higher amount of WCO was added. This is due to more sp^3 being formed as the reaction between WCO and zinc acetate has taken place for the formation of the Zn-OOC bond, CH_2 and CH_3 bonds in the nanocomposite which is in good agreement with the FTIR spectra observation. A broad 2D band at 2400 cm^{-1} was also recorded for the nanocomposite synthesized without WCO.

e) Surface Area and Porosity

BET nitrogen adsorption-desorption isotherms for CNTC/ZnO nanocomposites synthesized at various WCO contents (a) after the hydrothermal process and (b) after the calcination at 500 °C was studied. The effect of BET-specific surface area of the nanocomposites before and after the calcination treatment is also indicated in Figure 5(c).

All the adsorption-desorption isotherms of the nanocomposites before and after the calcination are dominated by Type IV (Figure 5(a) and (b)), indicating the mesoporous nature of the samples. This property is inherited from the mesoporous nature of the CNTC. As we know ZnO nanoparticles are only attached to the surface of the CNTC of the nanocomposite, therefore their presence will not very much alter the overall shape of the adsorption-desorption isotherms.

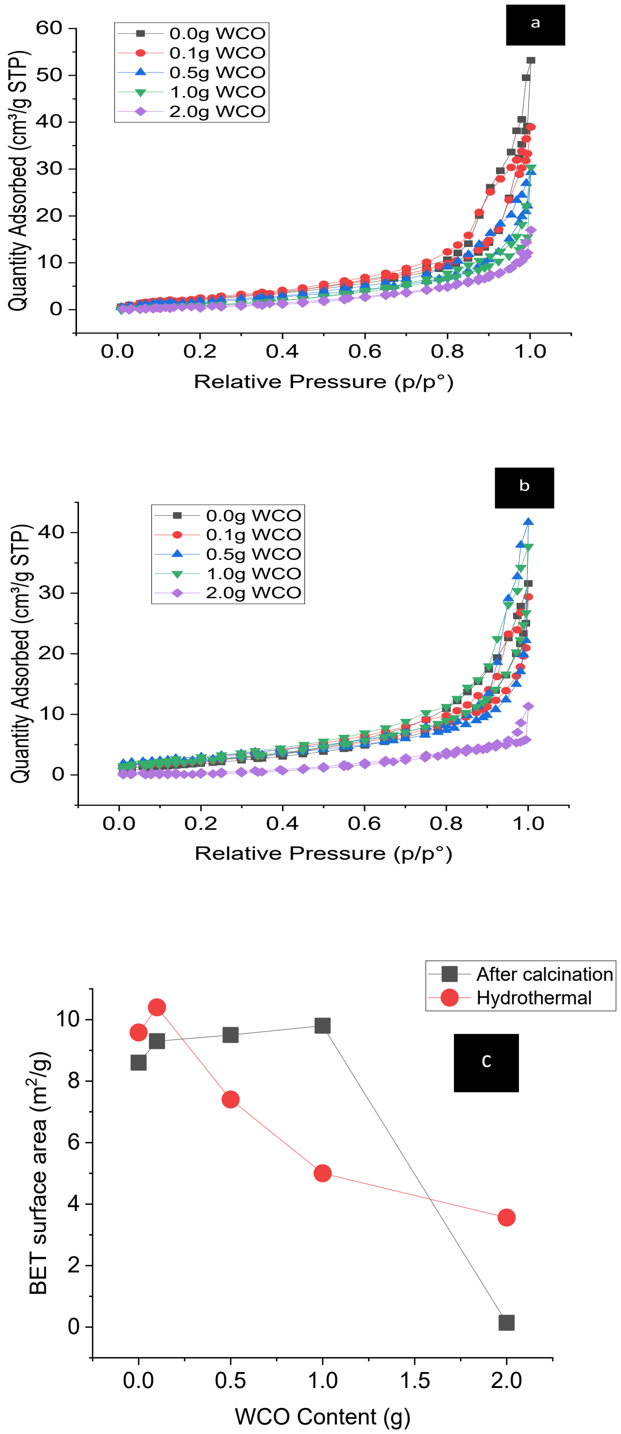

Figure 5: The BET adsorption-desorption isotherms of the CNTC/ZnO nanocomposites synthesized at various WCO contents; 0.0, 0.5, 1.0 and 2.0 g (w/w) (a) after the hydrothermal process, (b) after the calcination at 500 °C, and (c) the effect of their BET-specific surface area after the hydrothermal process and after the calcination at 500 °C

The BET-specific surface area of the nanocomposite synthesized without the addition of WCO has a surface area of 9.5 m^2/g and it reduced to about 8.5 m^2/g on calcination treatment at 500 °C. The addition of 0.1 g WCO resulted in a slightly higher surface area and a similar trend was observed when the sample was calcined at 500 °C.

Further addition of WCO from 0.5 to 2.0 g, resulted in the reduction of the SSA down to 4 m^2/g, however, after the calcination, the nanocomposite maintained an SSA of around 9 m^2/g except the one synthesized using 2.0 g WCO, in which the SSA reduced down to 0.1 m^2/g. This indicates that the removal of the biotemplate, WCO has not had much effect on the SSA of the resulting nanocomposites.

Conclusions

In this work, It can be seen that waste cooking oil played double roles in the preparation of the CNTC/ZnO nanocomposite, as a biotemplate as well as the carbon source for the synthesis of CNTC. The presence of WCO provided a nucleation site for the ZnO growth as indicated by the presence of the COO-Zn bond in the FTIR spectra and the presence of the ZnO and carbon phases as recorded in the XRD patterns. In addition, it was found that the concentrations of WCO also play a key factor in ZnO growth. At low concentrations of WCO, the morphological images showed the biotemplate acted as the shape modifier. On the other hand, at high concentrations of WCO, the defects became prominent due to the formation of the COO-Zn bond and the formation of the sp^3, in agreement with the increase of the I_D/I_G ratio of the Raman spectrum of the resulting nanocomposite.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Conflict of Interest

The authors declare there are no conflict of interest in this work.

Compliance with Ethical Standards

The work is compliant with ethical standards

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