Physicochemical Characterization of Candle Soot Functionalized with Nitric Acid

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Carbon nanoparticles (CNPs) have been identified as critical components in a variety of applications such as sensors, quantum dots, electrocatalysts, energy storage, and functional coatings. Candle soot can be used to produce uniform and efficient CNP materials. However, the known shortcomings, such as surface functionality and chemical stability have hindered the candle soot from being using as electrocatalysts. In this work, the synthesized of nitric acid functionalized candle soot (f-CS) will be compared with bare candle soot (CS) and wash candle soot (w-CS) in terms of physicochemical properties which to be used in electrochemical reaction. The nitric acid treatment was introduced into the candle soot surface to introduced oxygenated functionalities group and impeding the agglomeration and/or loss of active surface. The samples were evaluated using X-ray diffraction (XRD), Brunauer–Emmet–Teller (BET), field emission scanning electron microscopy (FESEM), and Raman analysis. After nitric acid treatment, the BET surface area has slightly reduced from 111.01 m^2/g to 95.66 m^2/g. These results demonstrated that oxygenated groups are incorporated into the carbon pore structure, blocking up the carbon pores. Experiments utilizing Raman demonstrated that functionalized candle soot has higher I_D/I_G ratio with value of 0.90 than bare soot with value of 0.82. Increased surface defects will give additional sites to anchor of metal particles, thereby increasing the number of metal-active sites. This f-CS will serve as a feasible basis material for an electrocatalysts, anode materials for energy storage, etc.

1. Introduction

Carbon-based materials have long been of great interest due to their distinctive physicochemical, electrical, mechanical, and chemical characteristics. This category consists of activated carbons, carbon nanofibers (Levitt et al. 2019), graphene (Khan et al. 2019), carbon nanotubes, and ordered mesoporous carbon materials (Rahman et al. 2021) . Potential applications for these materials include usage as catalyst supports (mostly for metals and their oxides), adsorbents for hydrophobic molecules and biomolecules, lithium-ion batteries (Chen et al. 2019), electrochemical capacitors (Levitt et al. 2019), and drug deliveries (Komur et al. 2017) . Candle burning is one of the simplest and most accessible methods for creating carbon nanoparticles. Candle soot is a very new, low-cost, and readily-available alternative to various other carbon-based materials. There is a perception that candle soot is an undesirable pollutant. However, Liu et al. (2007) discovered that it is a valuable source of carbon nanoparticles. Burning paraffin wax creates candle soot, that forms a fractal-like nanostructure of interconnected porous carbon. These carbon nanostructures have a high electrical conductivity, a large surface area, and a mesoporous structure (Mulay et al., 2019). Yu et al. (2021) previously discovered that candle soot has a mesoporous structure that enabled mass transfer and electrolyte/reactant access to active sites inside electrocatalysts. However, they frequently require prior modification because of their relatively inadequate chemical surface characteristics and limited number of functional groups.

Carbon-based materials are commonly treated with nitric acid for purification and/or functionalization. Nitric acid is often used to add oxygen-containing groups to the surface of carbonaceous materials. These groups serve as a starting point for adding more functions to carbonaceous materials. The attachment of organic molecules

and metal nanoparticles may be achieved by surface functionalization with O-containing groups acting as anchoring sites (Veizaga et al., 2019). Michal et al. (2018)   explored the effect of concentration nitric acid, temperature, and time of oxidation reaction of ordered mesoporous carbon (OMC) on the composition of functional groups. The highest concentration of functional groups in OMC like carboxyl groups, esters, lactones, and quinones was found to be achieved by oxidation in a 5 M nitric acid solution at 100 °C. Adding these oxygen-containing functional groups could significantly enhance metal dispersion, However, the mesoporous channels would be severely damaged by these strong oxidation reagents, and the pores would get blocked or collapse, limiting the opportunities of mesoporous carbon as a carbon support (Li et al., 2021). Thus, the structure of carbon materials was shown to be best maintained using low nitric acid concentration and low temperatures (Bazuła et al., 2008). By contrast, Öztürk and Yurtcan (2018) mentioned that the new catalytic active sites are created by these defects, which can improved the electronic structures and their adsorption strength of reactive intermediates. Recently, candle soot has been functionalized with oxygen-containing groups to improve the electrochemical characteristics of carbon nanoparticles (Justin Raj et al., 2016). Oxygen functional groups increased the surface area and pseudo capacitance of the candle soot electrode, leading to improved electrochemical properties. This demonstrates the possibility for functionalized candle soot to act as an electrocatalyst, anode materials in energy storage, etc.

In this research, the surface of candle soot was functionalized with nitric acid by adding oxygenated functional groups, therefore changing its characteristics, and preventing agglomeration and/or loss of active surface. The formation of functional groups in the candle soot is described in terms of the physicochemical properties.

2. Methodology

2.1 Materials

Pure wax candle with diameter of 1.7 cm and height of 23 cm (Lilin Jelita 1280, Malaysia) purchased from the local market. Ethanol absolute (99.5 %, Sigma Aldrich, USA) and nitric acid (HNO_3, 69 %, Merck, Germany) were used as received.

2.2 Collection of candle soot nanoparticles

A candle will be lighted in a basic laboratory setup. The candle soot (CS) is deposited on the ceramic lid while utilizing the direct-burning method. A mixture of ethanol and deionized water (1:1) will be sonicated with the collected soot, also known as CS, for 5 min at 37 kHz and 100 W. This washing process seeks to purge bare carbon soot of any residual contaminants and unburned hydrocarbons. The resulting washed candle soot (w-CS) will be dried overnight at 110 °C to remove any remaining moisture from the carbon soot.

2.3 Surface functionalization of candle soot

After washing, the candle soot will be functionalized by being refluxed in 1 M nitric acid (HNO_3) for 8 h at 100 °C (labelled as functionalized candle soot, or f-CS) (As in Figure 1). The acidity of the functionalized candle soot was neutralized by filtering and rinsing it with deionized water until the pH of the effluent was 7. After that, the candle soot was functionalized and dried in an oven at 60 °C for overnight to remove any remaining moisture.
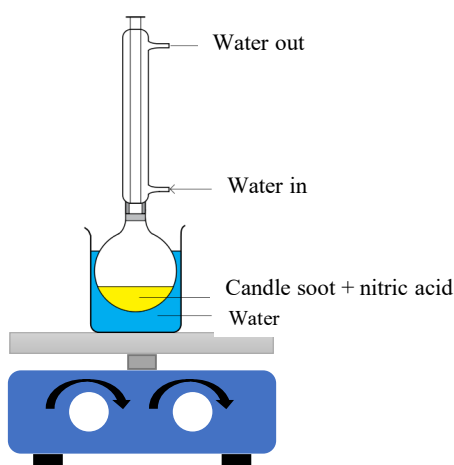

Figure 1: Schematic representation of candle soot functionalization with 1 M HNO₃

2.4 Characterization

With a Bruker AXS DB Advance diffractometer (CuKα radiation, λ= 0.154 nm), X-ray diffraction (XRD) patterns were recorded between 2° and 90°. The specific surface area of the samples was calculated using a Brunauer-Emmett-Teller (BET) analyzer with a Quantachrome type Autosorb-1. To ensure that no impurities or moisture were present in the samples before measurement, they were heated to 150 °C and purged with pure nitrogen gas overnight. The surface morphology analysis for the samples were carried out by field emission scanning electron microscopy (FESEM) (JEOL model no: JSM-7800F). A laser Raman micro spectrometer with a 532 nm excitation wavelength was used to analyze Raman spectra of the samples.

3. Results and discussion

3.1 Synthesis of surface functionalization of candle soot

The synthesis of functionalization of candle soot is depicted in Figure 2 using a schematic illustration. It is important to activate the graphitic surface, which contributes to the uniform dispersion and size control of the catalyst particles, because the surfaces of the synthesized candle soot are typically chemically inert. To improve their physicochemical properties, produced candle soot were subjected to an acidic treatment that altered their structure and surface chemistry. For efficient attachment of the metal nanoparticle for future works, hydrophilic groups (–COOH, –C=O, and –OH) were introduced into the candle soot by pretreatment with nitric acid. Since candle soot have a mesoporous structure, acids may more easily permeate the candle soot, opening the door to the development of more active sites than is possible with untreated candle soot (Karuppanan et al., 2018).
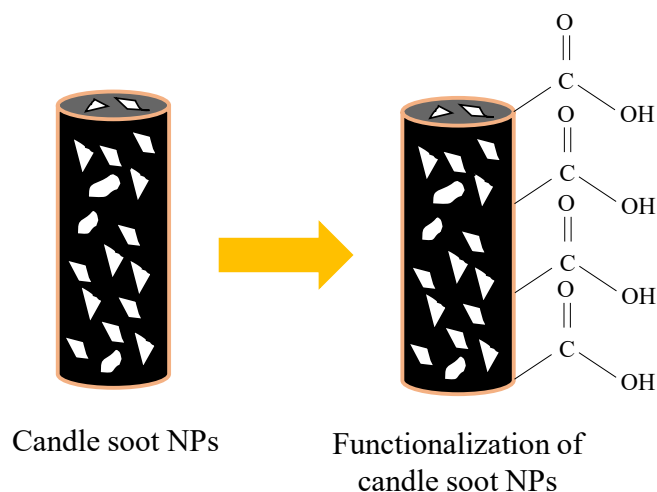

Figure 2: Schematic illustration of acid-functionalization of candle soot. Adapted from Karuppanan et al. (2018)

3.2 Structural and morphological studies

Figure 3 shows the X-ray diffraction (XRD) patterns of three samples, namely, CS, w-CS, and f-CS,. The XRD patterns show two prominent broad diffraction peaks at roughly 24.5° and 43.5°, which are indicative of the (002) and (100) planes of the graphitic carbon phase, respectively (Shi et al., 2020). When compared to the graphite XRD patterns on the JCPDS card (No-41-1487), there is a close match. The f-CS are primarily nanocrystalline, as seen by the broad peak located at 24.5°. The peak at 42.7° is primarily due to the interlayer scattering of graphene stacks, proving the presence of graphitic structure (Jache et al., 2012). In contrast, CS samples exhibit low and incoherent diffraction intensities, suggesting the presence of a considerable quantity of amorphous carbon and unburdened wax. The position of the peaks was altered following the functionalization procedure. This phenomenon is due to the integration of oxygenated groups into the structure of carbon soot (Carmo and Linardi, 2009). This demonstrates that candle soot was successfully functionalized using nitric acid.

The morphology of CS, w-CS, and f-CS was conducted on FESEM, which can be observed in Figure 4(a) to 4(c). The microscopic structures of the employed CS sample revealed that it was constituted of spherical carbon nanoparticles that had agglomerated into loose spongy frameworks. It is evident from Figure 4(c) that the surface and size of the nanoparticles changes significantly after nitric acid treatment. It has been shown that

functionalization of nitric acid can reduce particle size and increase porosity in materials. Also, the structure of the candle soot was not compromised in any way.
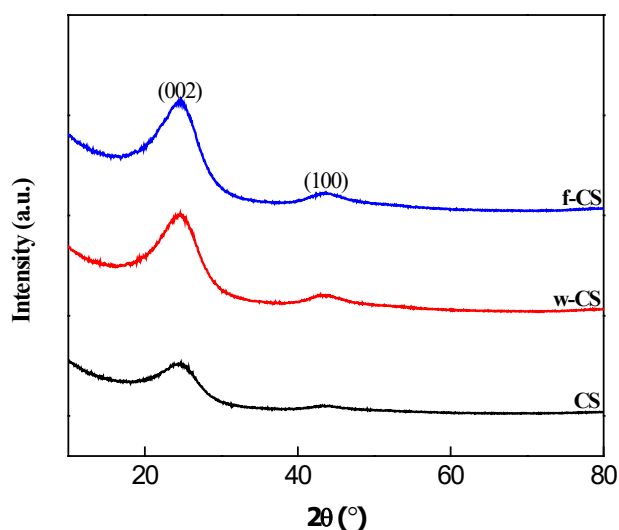

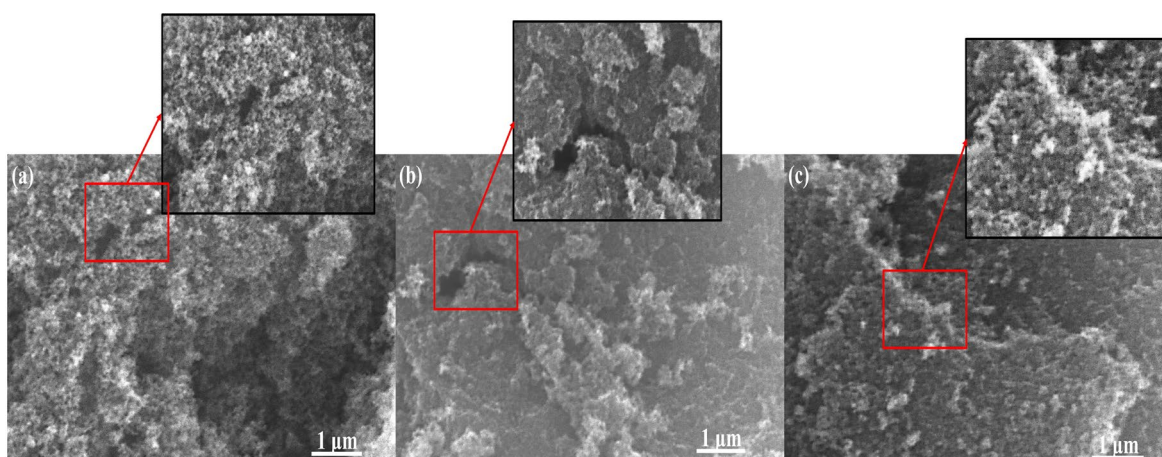Figure 3: X-ray diffraction of candle soot samples namely the CS, w-CS, and f-CS

Figure 4: FESEM micrograph of (a) CS, (b) w-CS, and (c) f-CS samples with a magnification of 15, 000 X

3.3 Surface specific area

In this study, the surface specific area of candle soot before and after treatment with nitric acid were examined since the surface area of carbon materials influences several physicochemical properties. The parameters for the pore structure of the three samples are listed in Table 1. As indicated in Table 1, the surface area of candle soot has decreased from 111.01 to 95.66 m^2/g following modification. The functionalization process blocks off some of the micropores, which contributes to the reduction in these values. It is likely that the oxygen functional groups are located near the entrances of carbon pore structures, resulting in a reduction in their area and volume (Marciniak et al., 2018). There is a suggestion that with functionalization, oxygen surface groups attached at the entrance of micropores prevent species from diffusing within. So, it is desirable as it can prevent the metal catalyst to fill up the micropores of the candle soot. According to Carmo and Linardi (2009), micropores filled with metal catalyst can restrict reactant access to active sites.

Table 1: Textural properties of CS and f-CS

Sample	S_{BET} (m^2/g)	V_{Total} (cm^3/g)	D_{Pore} (nm)
CS	111.01	0.183	3.32
f-CS	95.66	0.152	5.48

3.4 Raman analysis

Candle soot structure crystal disorder and bonding properties are investigated using Raman spectroscopy. Figure 5 indicates the Raman spectra of candle soot before and after treatment with nitric acid. There are two prominent peaks, one at ~1,340 cm^{-1} (the D band) and the other at ~1,590 cm^{-1} (the G band) that are characteristic of graphite. The D peak is primarily caused by flaws in the carbon support (Sanchez-Sanchez et al., 2013). When there are more defects on the surface, the D peak becomes more prominent. There will be more metal-active sites because more surface defects will be available for attaching metal particles. The G peak indicates the degree of graphitization of candle soot. There is a positive correlation between the degree of graphitization and the intensity of the G peak. The number of defect sites is decreased, and the degree of graphitization is improved by the acid-functionalization. The ratio of G to D band intensities (I_D/I_G) is frequently used to define the defect density in carbon and graphitic materials. The I_D/I_G of f-CS (0.88) is more than CS (0.85). It is most likely the outcome of carbon structure defects caused by functionalization (Zhong et al., 2018). The additional defects could enhance the electrocatalytic activity of the material.
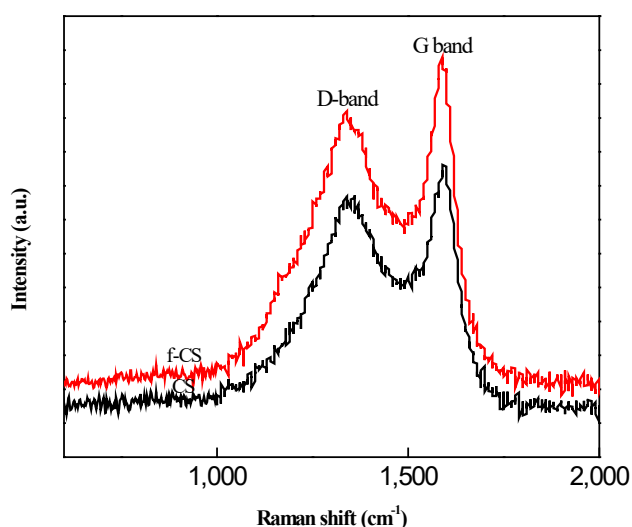

Figure 5: Raman spectra of CS and f-CS samples

4. Conclusions

In summary, the effect of nitric acid treatment on the physicochemical parameters of candle soot, including the structural and morphological, surface specific area, and defect density on surface of candle soot were evaluated. On a case-by-case basis, the treatment of candle soot materials with nitric acid results in vastly varied physicochemical modifications. The BET data indicated that the specific surface area of the carbon soot was reduced by 14 % following functionalization, indicating that the treatment employed caused significant modifications to the carbon soot structure. The XRD data demonstrated that the location of the peaks changed following functionalization. This phenomenon is due to the integration of oxygenated groups into the structure of carbon soot. In order to enhance the interaction between the metal nanoparticles and the carbon soot, it is proposed that the presence of these functional groups might act as anchor site on the carbon soot. This novel approach of nitric acid functionalization offers an innovation for the enhancement of candle soot properties to be an electrocatalyst, anode materials for energy storage, etc.

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