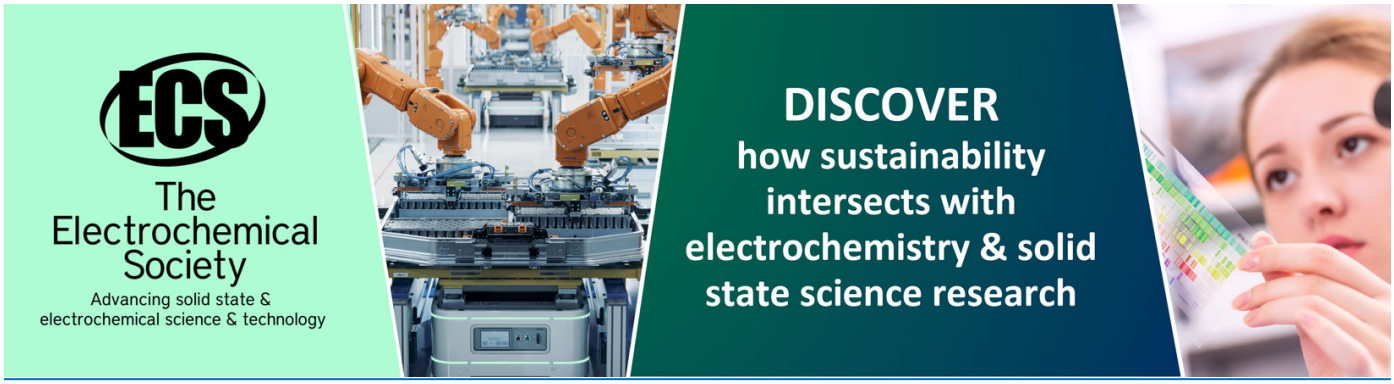
Green Synthesis of Silicon Carbide Nanowhiskers by Microwave Heating of Blends of Palm Kernel Shell and Silica



Green Synthesis of Silicon Carbide Nanowhiskers by Microwave Heating of Blends of Palm Kernel Shell and Silica

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Abstract. Silicon carbide nanomaterials especially silicon carbide nanowhiskers (SiCNWs) has been known for its excellent properties such as high thermal stability, good chemical inertness and excellent electronic properties. In this paper, a green synthesis of SiCNWs by microwave heating of blends of palm kernel shell (PKS) and silica was presented. The effect of ratio of PKS and silica on the synthesis process was also studied and reported. Blends of PKS and silica in different ratio were mixed homogenously in ultrasonic bath for 2 hours using ethanol as liquid medium. The blends were then dried on hotplate to remove the ethanol and compressed into pellets form.. Synthesis was conducted in 2.45 GHz multimode cavity at 1400 °C for 40 minutes. X-ray diffraction revealed that β–SiC was detected for samples synthesized from blends with ratio of PKS to silica of 5:1 and 7:1. FESEM images also show that SiCNWs with the average diameter of 70 nm were successfully formed from blends with ratio of PKS to silica of 5:1 and 7:1. A vapour-liquid-solid (VLS) mechanism was proposed to explain the growth of SiCNWs from blends of PKS and silica.

1. Introduction

Silicon carbide (SiC) is one of the non-oxide ceramic materials that have superior properties such as high hardness, low thermal expansion, good thermal resistance, excellent oxidation resistance and wear resistance [1–3]. The superior properties of the SiC are due to the strong covalent bonding between Si and C [4]. By reducing the size of SiC to nano-scale, the properties of SiC can be enhanced due to the quantum confinement effect conductivity, high corrosion and increased relative surface area [5]. SiC nano-materials can be applied in many fields such as nano-electronic [6], metal matrix composite (MMC) [1], optoelectronic device [5] and sensor [6].

Acheson process is the first method used for the synthesis of SiC. This method needs very long heating duration and thus large energy consumption. The SiC produced are coarse and need secondary process such as milling process to reduce the particle size. Besides that, contaminations always occurred during milling process [7]. Therefore, different methods for the synthesis of SiC were developed. These included sol-gel method [1], pulsed laser deposition technique [8], chemical vapour deposition method [9] and microwave synthesis method [10]. Recently, microwave heating is widely

used to synthesize inorganic materials such as SiC [11]. Comparing to conventional heating which involves transfer of heat energy by conduction, convection and radiation, microwave heating transfers energy through the molecular-level interactions between electromagnetic field and materials, so it can heat materials volumetrically and reduce the heating duration, energy consumption and lead to high yielding [10,12–14]

The common raw materials used for the synthesis of SiC are high purity carbon such as graphite and silica. Researches were conducted to investigate the feasibility of green synthesis of SiC from industrial waste such as rice husks [15], bleached wood pulp [16], coconut fibres [17] and bamboo leaves [18]. Currently, Malaysia is the second largest palm oil production country in the world. Palm kernel shells (PKS) are the shell fractions left after the palm kernels are crushed in palm oil mill. The characteristic of PKS such as high carbon (around 75 wt %) [19], but low inorganic contents show that PKS is suitable raw material for the synthesis of SiC nano-materials.

In this paper, PKS was used as carbon source for the synthesis of SiC nanowhiskers (SiCNWs). The use of PKS for the synthesis of SiCNWs can solve the disposal issue of PKS. To the best of the authors' knowledge, no study on the synthesis of SiCNWs using PKS as raw materials was reported. In this study, PKS was first pyrolysed to carbon by microwaves heating and reacted with silica for the formation of SiCNWs. The as synthesized SiCNWs were characterized by using FESEM and XRD. The effect of ratio of PKS to silica on the synthesis of SiCNWs was also studied and reported. A mechanism of formation of SiCNWs by microwaves heating of blends of PKS and silica was also proposed.

2. Experimental

2.1. Preparation of Blends of PKS and Silica

Silica powders (Sigma Aldrich, 99.5% purity, 325 mesh) and PKS powder (DRPTS Manufacturing Sdn. Bhd., 63 μm of particle size) were used as raw materials in this study. Previous study suggested that the carbon to silica ratio to be slightly higher than the stoichiometric ratio (3:1) to obtain phase-pure SiC [3]. However, PKS was reported to contain only 75 wt % of carbon. Therefore, PKS and silica were mixed in four different molar ratio of PKS/SiO_2 (which are 1:1, 3:1, 5:1 and 7:1) to study the effect of molar ratio of PKS/SiO_2 to the synthesis of SiC. A total mass of each sample was 2g to enable the pelletizing of samples using hydraulic hand press. The powders were mixed in ultrasonic mixing bath for 2 hours using ethanol as liquid medium. The homogeneously mixed blend with ethanol was dried using hot plate to remove the ethanol. The fully dried blends were pressed into a 3 mm thickness die by using hydraulic hand press to form pellet. The pressure used to compact the powder was approximately 312 MPa. The pellet was then placed in a silica crucible filled with silica sand, graphite and SiC susceptors. Silica is transparent to microwave and thus does not absorb microwave. Silica crucible and sand acted as thermal insulator to reduce the heat loss. Graphite and SiC susceptors are good microwaves absorbers and can increase the heating rate during microwave heating process.

2.2. Synthesis of SiCNWs by Microwaves Heating

The synthesis of SiCNWs was conducted in a 2.45GHz multimode cavity microwave furnace (ChangSha Syno-Therm Co. Ltd., MW-L0316V) with a maximum operating power of 3kW. The set up as shown in Figure 1 was placed into the microwave cavity. The temperature of the pellet was measured by a pyrometer that was placed above the pellet. Before the heating process, the microwaves cavity was vacuumed and argon gas was allowed to flow continuously into the cavity during the entire heating process. The heating temperature was set to 1400 ºC with a heating rate of 30 ºC/min. The heating duration was 40 minutes. After the heating process, the pellet was cooled in the microwave cavity naturally until it reached room temperature [11].

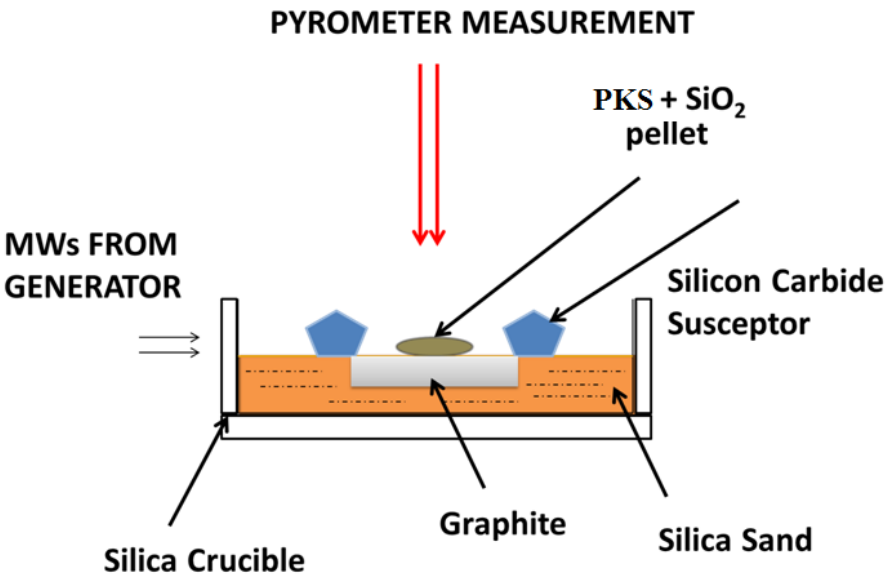

Figure 1. Schematic Diagram of Setup Within Microwave Cavity.

2.3. Sample Characterization

The samples were characterized by field emission scanning electron microscopy (FESEM, Nova Nano SEM 450) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford X-Max) to investigated the morphology and elemental composition of the samples. X-ray diffraction (XRD, Shimadzu, XRD-6000) was used to identify the phase and the composition of the samples. The diffraction patterns were recorded using Cu Kα radiation over a 2θ range of 20º to 80º with step size of 0.02º.

3. Results and discussion

Figure 2 shows the XRD patterns of PKS and blends of PKS and SiO_2 in different ratios that were subjected to microwaves heating. For XRD pattern of PKS, a broad peak of carbon was observed, indicating the amorphous state of carbon in PKS. For the XRD patterns of blends of PKS and SiO_2 in different ratios that were subjected to microwaves heating, peaks corresponding to SiO_2, C, and SiC were observed. The SiC peaks were located around 35.5 º, 59.9º and 71.6º, corresponding to plane (111), (220) and (331) of β-SiC, respectively [3, 20]. By increased the ratio of PKS to SiO_2 from 1:1 to 7:1, the intensity of β-SiC peak in XRD patterns increased, indicating the amount of β-SiC increased with the increasing ratio of PKS to SiO_2. This is in good agreement with the observations reported by Kahar et al. [21]. Peaks attributed to C and SiO_2 were also observed for all samples, indicating synthesis process was incomplete.

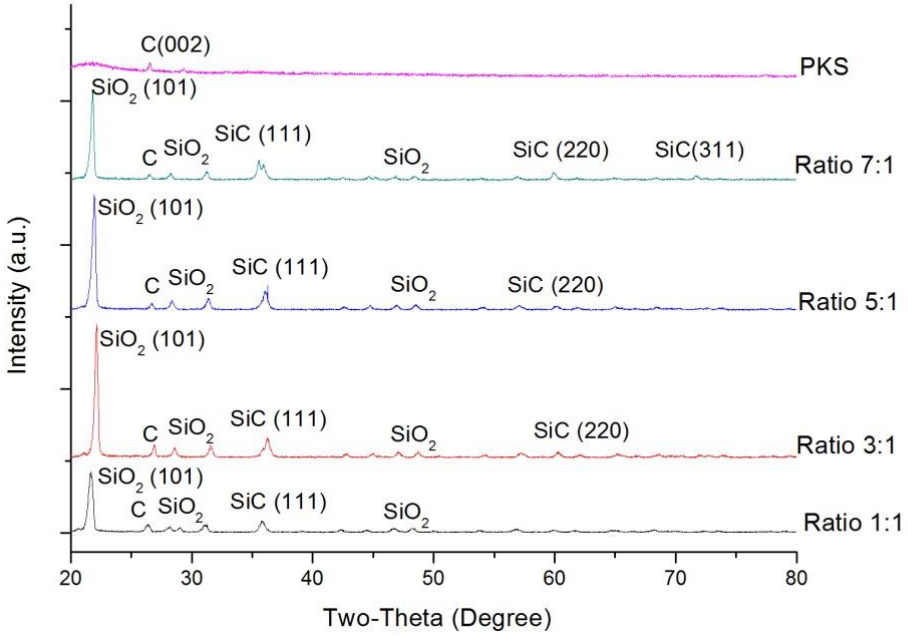

Figure 2. XRD Patterns of PKS and Blends of PKS:SiO_2 Subjected to Microwave Heating in the Ratio of 1:1, 3:1, 5:1 and 7:1.

Figure 3 shows the FESEM images of PKS and blends of PKS and SiO_2 in different ratios that were subjected to microwaves heating. As in Figure 3 (a), PKS were aggregations of irregular particles. From Figure 3 (b) to (e), it can be seen that as the ratio of PKS to SiO_2 increased, the occurrence of SiCNWs increased. This is in good agreement with the XRD patterns in Figure 2, which shows that the intensity of SiC peaks increased with the increasing ratio of PKS to SiO_2. The diameter of the SiCNWs was in the range of 50-80 nm. This is due to the carbon content in PKS is approximately 75 wt % [19]. Thus, the ratio of PKS:SiO_2 of 5:1 and 7:1 are equivalent to C:SiO_2 ratio of 3.75:1 and 5.25:1, respectively. Study conducted by Kahar et al suggested C: SiO_2 ratio of slightly higher than 3:1 is favourable for the synthesis of SiC [21]. Furthermore, excess carbon in the raw materials can create a reducing atmosphere to prevent the oxidation of products and to prevent the sintering of formed SiC into aggregates. It can also be observed in Figure 3 (d) that droplet cap was found at the tip of the SiCNWs. The diameter of the droplet cap was approximately 80 nm. Typically, the nanowhiskers or nanowires with a droplet on the tips were synthesized through vapour-liquid-solid (VLS) mechanism [22]. In this study, SiCNWs synthesised by microwave heating of blends of PKS and SiO_2 was explained by VLS mechanism.

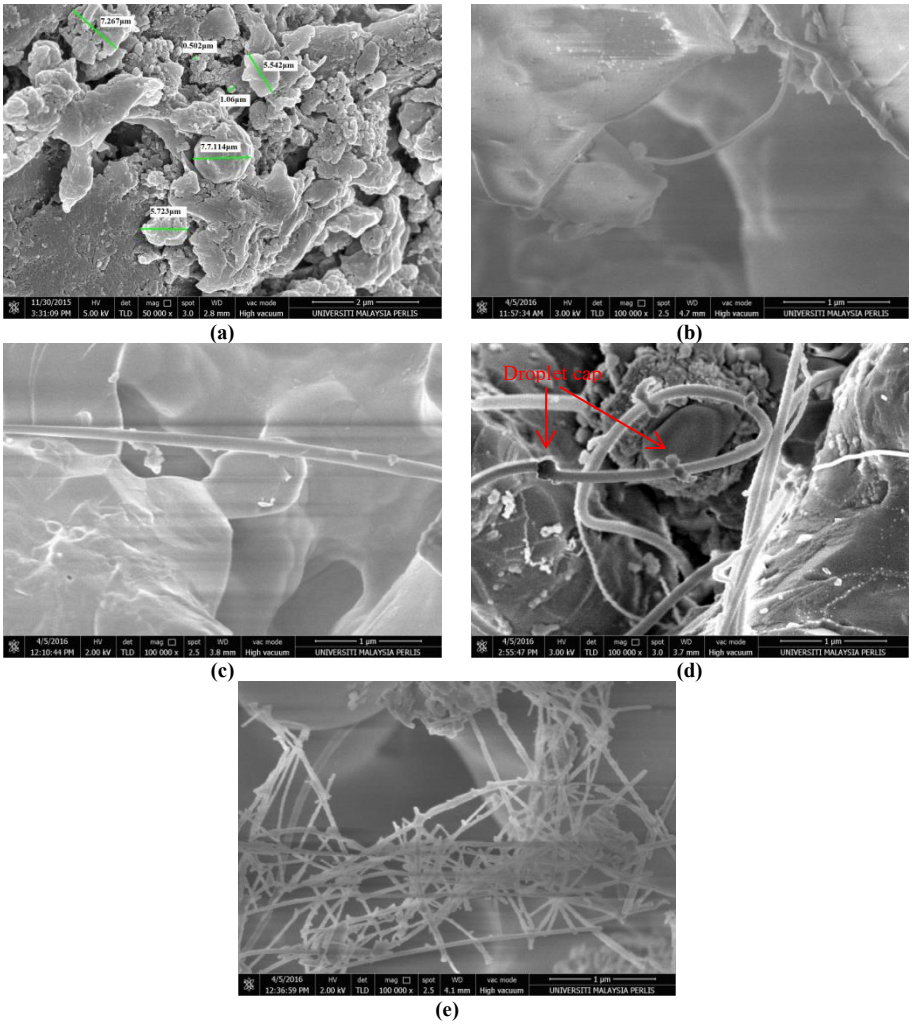

Figure 3. FE-SEM Images of the (a) PKS Powder and the Mixture of PKS:SiO_2 Subjected to Microwave Heating in the Ratio of (b) 1:1, (c) 3:1, (d) 5:1 and (e) 7:1.

The overall reaction of formation for SiC through carbothermal reduction is generally written as in Equation 1.

$$SiO_2\ (s) + 3C\ (s) = SiC\ (s) + 2CO\ (g) \quad (1)$$

Figure 4 (a) shows the blends PKS and SiO_2 subjected to microwave heating. When the temperature increased to 500 °C to 600 °C in the microwave cavity, the PKS pyrolyzed and formed carbon as in Figure 4 (b). As the temperature further increased, VLS mechanism occurred. The growth mechanism of VLS consisted of two stages. First stage involved the nucleation and growth of eutectic alloy droplets. When the alloy melted, it absorbed SiO and CO gas to form a nano-liquid alloy droplet [23,24]. The reaction in Equation 2 has produced SiO and CO gas. Second step involved the growth of the nanowire or whisker from supersaturated liquid at the liquid/solid interface as in Figure 4 (c). The nuclei of SiC formed from the supersaturated alloy liquid. The nanowhiskers continued to grow in length as the SiO and CO gases dissolved into the liquid alloy and finally SiCNWs were formed as in Figure 4 (d). As cooled from deposition temperature, typically a solidified spherical droplet formed on the tip of the nanowhiskers. In this study, no catalyst was added into the sample during the synthesis process. The transition metals that acted as catalyst may be found in PKS powder as impurity as

reported by Edmund et al. [19] and Dagwa et al. [25] where they found that there was small amount of iron and potassium in PKS which may act as catalyst.

$$SiO_2\ (s) + C\ (s) = SiO\ (g) + CO\ (g) \quad (2)$$

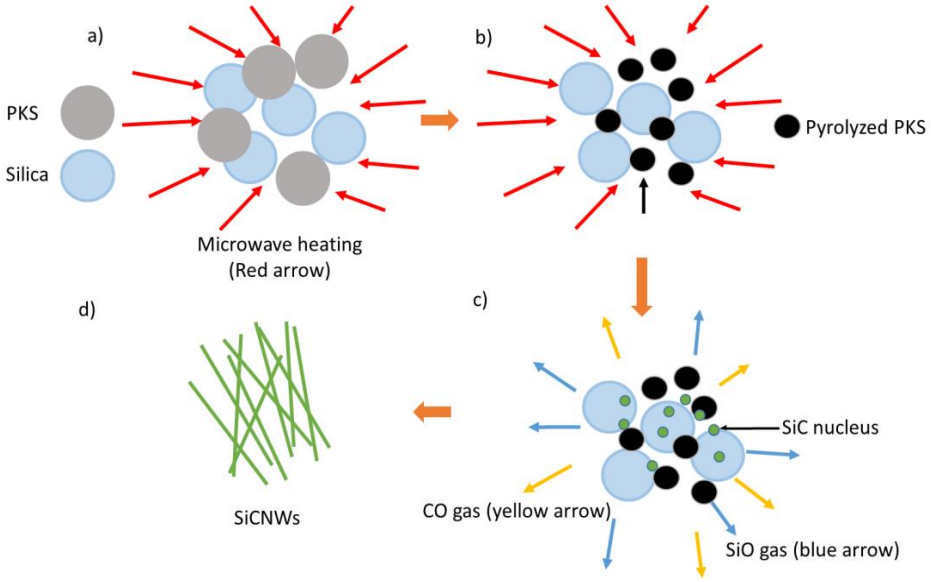

Figure 4. Growth Mechanism of SiCNWs by Microwave Heating of Blends of PKS and SiO_2.

4. Conclusion

In conclusion, β- SiCNWs were successfully synthesized by microwave heating of blends of PKS and SiO_2 at 1400 °C for 40 minutes in a microwave furnace. The effect of ratio of PKS to SiO_2 in the blends to the synthesis of β-SiCNWs was studied. SiCNWs were characterized by using X-ray diffraction and field emission scanning electron microscopy. PKS to SiO_2 ratio of 5:1 was found to be suitable for the synthesis of β-SiCNWs by microwave heating of blend of PKS and SiO_2. A VLS growth mechanism of β-SiCNWs by microwave heating of blends of PKS and SiO_2 was proposed.

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