Carbon Nanostructures Grown from Waste Latex via Chemical Vapor Deposition

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Abstract

In this work, CNS were successfully synthesized using waste latex from natural rubber gloves as carbon source via chemical vapor deposition. The synthesized process has been done at reaction temperature of 700˚C using iron oxide as catalyst. The CNS characterization were investigated by atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDS) and Raman spectrum techniques. It was found that the obtained carbon material existed in the form of nanotubes, fibers and nanocapsules with diameter of 5 - 20 nm. The I_G/I_D value was found to be approximately 0.84, indicating CNS in the samples were not well crystalline and contain defects. HRTEM images and EDS results reveal non-uniform of large catalyst size and impurities of carbon source might lead to less population of grown CNTs. This study demonstrates that waste latex can be an alternative and inexpensive carbon source for CNS production and promotes green technology.

Keywords: carbon nanostructures, waste latex, natural rubber

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Introduction

Since the main revelation in 1980s, carbon nanomaterials (CNMs) such as fullerenes, carbon nanotubes (CNTs), carbon nanofibers (CNFs) and graphene have been in the scientific spotlight due to their extraordinary mechanical, electrical, chemical, and thermal properties [1,2]. Their unique nanostructure holds incredibly guarantee for various potential technological applications such as nanowires and interconnects in nano-scale electronic devices, water treatments and thermal management [3-5]. Many efforts have been made to find the best synthesis techniques to produce high quality CNMs based on their target applications such as ion irradiation, laser ablation and arc discharge [6-8]. Among them, chemical vapor deposition (CVD) techniques are considered one of the best because of their economically viable and compatible process can be significant for industrial scale applications.

Conventionally, CNMs has been synthesized using petroleum based carbonaceous precursors such as methane and acetylene as the primary carbon sources [1,9]. On the other hands, solid and liquid carbon sources, such as camphor and ethanol have been investigated for CNMs synthesis as a possible carbon sources, considering the advantages of simple and controllable CVD process [10-11]. Recently, the idea of turning waste into wealth are gaining more attention in promoting green technology as well as green economy. For example, alternative carbon precursor from waste materials such as chicken fat, waste plastics, food and insects can be directly placed in the CVD system to produce graphene [12–14]. CNTs also have been reported to be synthesized from vulcanized scrap rubber, styrene butadiene rubber (SBR) and tire [15–17]. In this regard, our attention has been drawn to the feasibility of using waste latex, namely natural rubber (NR) glove as a potential carbon source to produce carbon nanostructures (CNS) and thereby converting waste into high value-added product. Natural rubber is a polymer of isoprene (also known as 2-methylbuta-1,3-diene) with the chemical formula $(C_5H_8)_n$, which means it is made of many thousands of basic C_5H_8 units (the monomer of isoprene) loosely joined to make long and tangled chains. The rich of hydrocarbon content are favorable to utilize them as a carbon precursor for CNS production.

The microscope such as atomic force microscope (AFM), scanning electron microscope (SEM) and transmission electron microscope (TEM) offers a unique opportunity to study the surface morphology, structural behavior, arrangements of the atoms on the surface as well as defect structures at nanometer scale. For example, the role of catalyst in CNMs formation have been explored by high-resolution TEM. Fe was reported to be the most efficient catalyst in term of quality of CNTs compared other transition metals [18]. In contrast, Au and Ag was found to be difficult to produce higher degree crystallinity of graphitic layers compared to Cu and Pt due to low their carbon solubility and melting temperature [19-22]. This information appears to play crucial roles in the formation process of CNMs, although the formation mechanism is not yet completely understood. Presumably, the key to further understanding of the formation mechanism can be achieve by revealing the complex nanostructure of CNMs through a detailed microscopy observations process. In this work, the focus is on the surface morphology and atomic resolution structures of CNS produced via CVD. The purpose of the present study is to investigate the CNS synthesized from rarely used carbon precursor: waste NR gloves using several microscopy techniques to identify their possibilities as CNMs precursor candidate.

Materials and Methods

CNS fabrication were conducted in a horizontal quartz tube furnace with diameter of 9.8 cm and in 100 cm length. 0.5 g of the iron oxide (Fe_3O_4) was dispersed in the center of ceramic boat which was then placed at the center of horizontal quartz tube furnace as catalyst for CNS synthesis. Solid waste laboratory NR gloves is used as carbon source for this experiment. 10 g of waste NR gloves was loaded into twin neck round bottom flask and connected to the pipe tubing gas with argon flow with heating mantle temperature at 380 °C. The deposition furnace was heated to 700°C with argon gas supplied at 150 cc/min, continuously. When the temperature was stable at 700°C, the precursor pipe tubing gas was turned-on. The CNS synthesis was carried out for 30 min. After the completion of the synthesis, the furnace was allowed to cool down to room temperature. The sample was characterized using atomic force microscopy (AFM: BRUKER CREST Dimension Edge), Raman spectroscopy (NRS-4100; JASCO laser Raman spectrometer with a laser excitation wavelength of 532.08 nm), field emission scanning electron microscopy (FESEM: NOVA NANOSEM 230) and transmission electron microscopy TEM (JEOL JEM 2100, operated at 200 kV) along with an Energy-dispersive X-ray (EDX) analyzer.

Results and Discussion

In the present work, the growth of CNS from waste NR gloves on Fe_3O_4 powder by CVD is demonstrated. The structural analysis of synthesized CNS was performed by AFM, SEM, and TEM. While for elemental analysis, the sample were characterized by EDX and selected area electron diffraction (SAED) pattern.

Surface topography

AFM is a convenient instrument for studying surfaces and has been utilized to provide qualitative and quantitative information regarding the topography of CNS at the nanometer scale. AFM allows for the determination of roughness parameters that can be calculated for the sample surface. The value showed were R_a and R_q, which indicates average roughness and root-mean square roughness, respectively. According to the AFM images (Fig.4a-b), CNS synthesized from waste latex exhibited the surface morphology with a rough appearance of R_q = 6.49 mV, R_a = 5 mV and R_q = 61 mV, R_a = 49.2 mV, respectively. Meanwhile the references (typical CNTs sample) exhibited a smoother surface of R_q = 2.79 mV, R_a = 2.2 mV and R_q = 2.49 mV, R_a = 1.93 mV, respectively. The presence of the precursor from waste NR gloves appears to favor an increased surface roughness, which is probably due to the complex chemical compound of hydrocarbon compared to ethanol to promote carbon diffusion process on the catalyst [23]. Agglomeration of iron oxide particles due to high reaction temperature also might be the reason that effect the roughness.

Surface morphology

Surface morphology of CNS was investigated by SEM and FESEM. Figure 2 shows a low magnification SEM image observed by SEM system (JCM-6000; JEOL) for comparison purposes. The results were comparable with the AFM images (Fig. 1(a-b), which indicates the consistency of results in both measurement methods. Figure 3 shows the morphologies of CNS synthesized using iron oxide catalyst at several different measurement spots. The magnified images of CNTs and carbon fibers are shown in Figure 3 (b) and (c) respectively. Figure 3 (d-e) shows different observation area, which reveal less distribution of nanotubes / fiber structure with the presence number of iron encapsulated graphite and un-reacted catalyst particles. The sample also had revealed a densely packed particles of different irregular sizes appear with strong necking between the neighbor particles. Figure 3(b-c) shows the CNS size and diameter. CNTs catalyzed by iron oxide nanoparticles have small diameter ranged at 16.9 - 89 nm. The diameter of carbon fiber was above 198.5 nm. The nanotubes were also severely crooked, obviously mixed with impurities namely amorphous carbon (a-C) and non-tubular carbon structures. There were also iron encapsulated graphite and agglomerated iron oxide with average particles size in range of 100 – 500 nm. It is found that the current synthesis parameter such as reaction temperature of 700°C gave low population of fibrous structure leaving large catalyst particles.

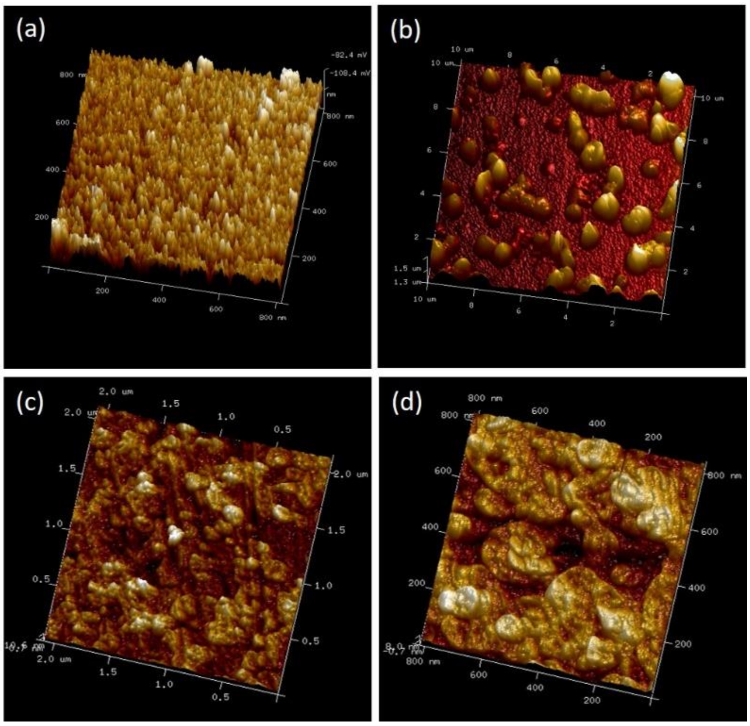

Figure 1. AFM topography images of CNS on iron oxide powder. (a-b) represent CNS produce from waste NR latex at different measurement point, while (c-d) are references images of typical CNTs produce by ethanol, respectively.

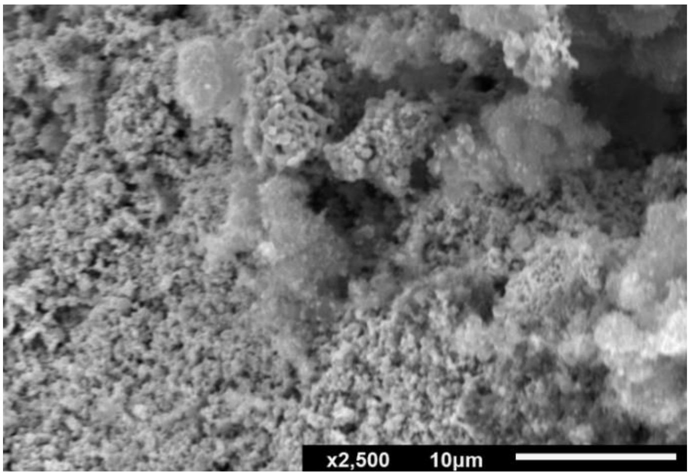

Figure 2. SEM images of CNS on iron oxide powder. Produced from waste NR latex.

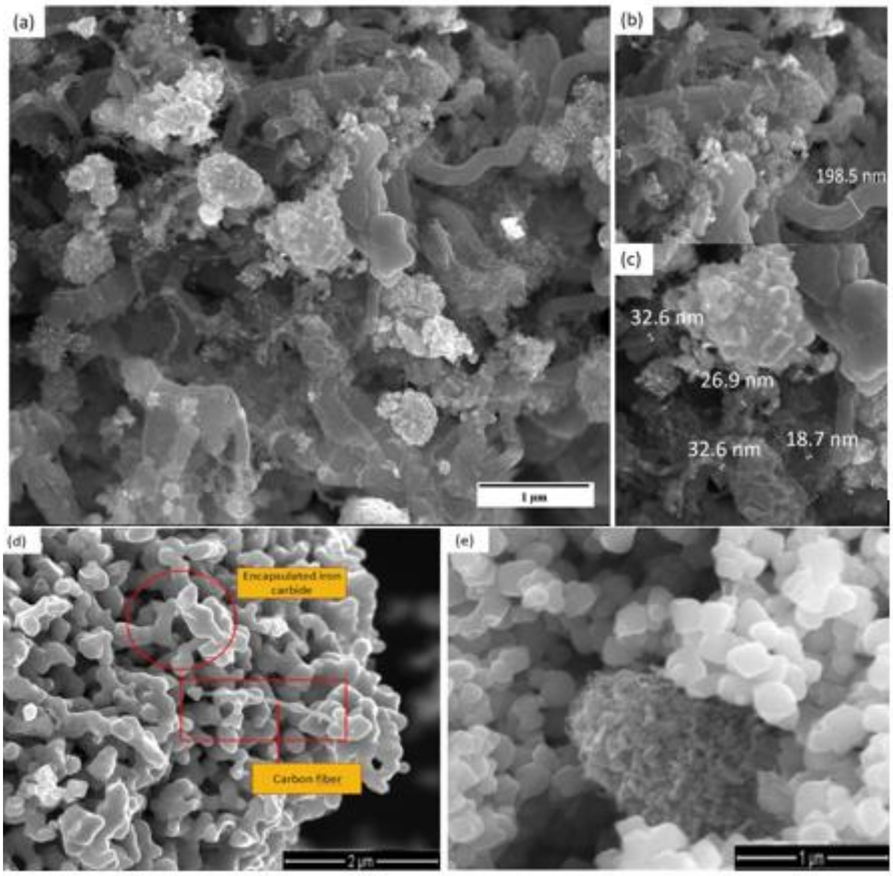

Figure 3. FESEM images of CNS synthesized using iron oxide catalyst (a) carbon fiber / CNTs spotted, (b)-(c) inset of (a), and (d)-(e) bundled iron carbide and CNTs / carbon fiber.

Raman spectroscopy

Figure 4 shows the results of Raman spectroscopy for CNS to study their crystallinity, taken from 2 different measurement spots of the same sample. The peaks in the Raman spectra of the CNS were separated by curve fitting using Gaussian functions to obtain the integrated intensity ratio I_G/I_D. The well separated two Raman peaks at 1312, 1344 cm^{-1} for D peaks and at 1587, 1601 cm^{-1} for G peaks was observed for spot (a) and (b), respectively. The I_G/I_D value was found to be approximately 0.83 and 0.84, respectively, which value are almost comparable for both measurement spot. Our results indicated that the CNTs in the samples were not well crystalline and contain many defects. There was no sign of low frequency radial breathing mode (RBM) peaks detected indicating non-existent of single-walled CNT (SWCNT) [24].

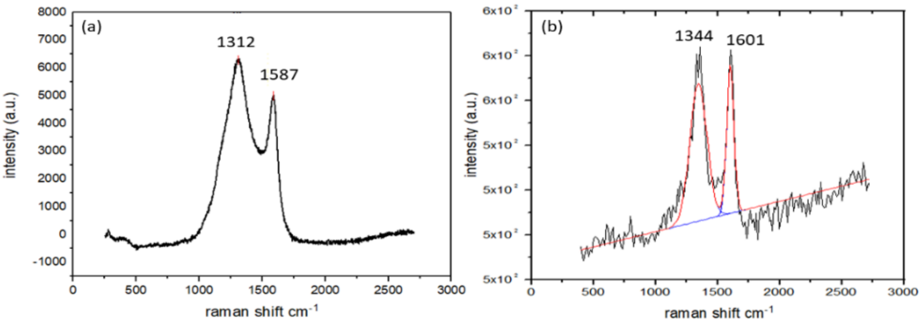

Figure 4. Typical Raman spectra of CNS synthesized using iron oxide catalyst at different measurement point (a) and (b).

Structural analysis

The utmost appropriate method to analyses the composition of the CNS is by using TEM. Figure 5 shows TEM observation results of the CNS from waste NR gloves. The TEM image reported in Fig. 5a depicts an overview of the sample taken at low magnification. The catalyst nanoparticles display non-uniform distribution of CNS is clearly seen grow on the catalyst. High magnification of the image (Fig. 5b-d) shows an image of the CNS in form of Fe encapsulated graphite. Carbon supply from waste NR gloves successfully diffuse on the catalyst surface, forming a graphitic layer. With increasing of reaction temperature, catalyst nanoparticles were half evaporated, leaving hollow structure of CNS. The process was clearer in Fig 5 (e-i), where the graphitic layer was separated from the catalyst, as reveal in Fig 5(e) in form of graphene layer and Fig 5(f-i) in form of hollow structure of CNTs and nano-capsule, respectively. The diameter of the hollow structure of CNT and nanocapsules were around 5 - 20 nm in average. It was reported that that larger nanoparticles are unable to catalyze the CNT growth effectively [25]. Therefore, the inconsistence in particle size of the used catalyst might affect the population of the growth of CNTs. This will lead to other forms of carbon structure such as carbon fiber or Fe encapsulated graphite, in agreement with FESEM results as shown in Fig. 3.

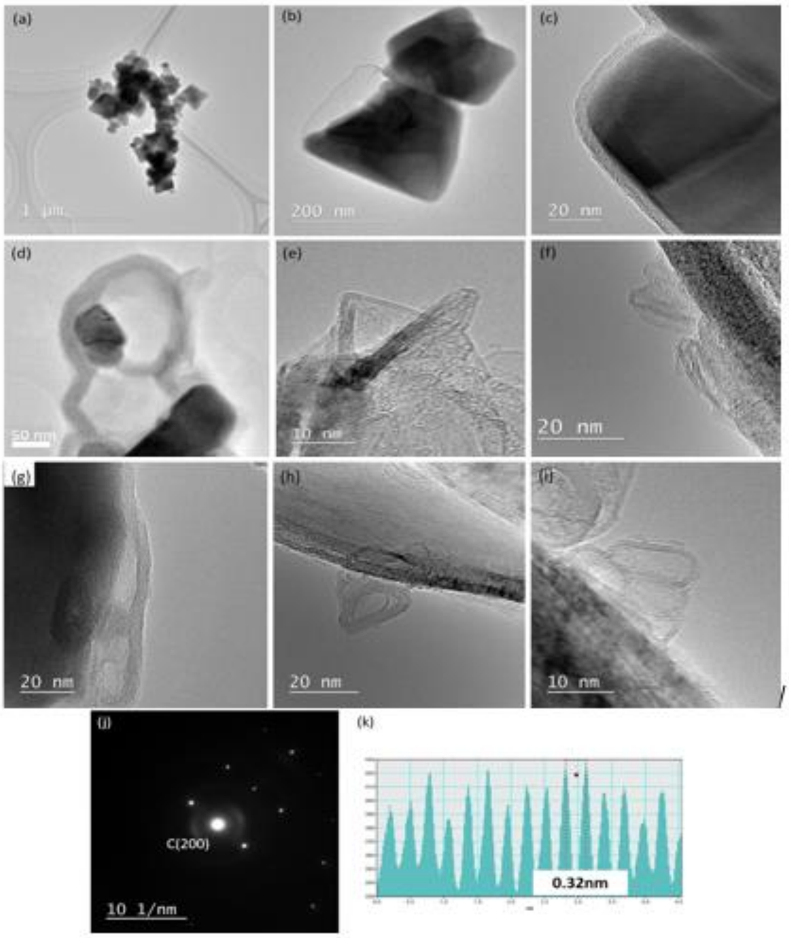

Figure 5. TEM images of the CNS synthesized using iron oxide catalyst. (a) Low-magnification TEM image. High-magnification TEM images of the CNS (b-d) Fe encapsulated graphite (e) graphene layer and (f-i) hollow CNTs and nano-capsule, respectively. (j-i) Corresponding SAED pattern and lattice profile.

The crystallinity of the CNTs was examined by HRTEM equipped with selected area electron diffraction (SAED) system together with lattice profiler as shown in Fig. 5(j, k), respectively. The characteristic 0.32 nm inter-wall spacing of the CNS is given in Fig. 5(k) and the ring-like pattern in SAED in Fig. 5(j) shows the (002) rings planes indicate the graphitic walls with nearby high crystallinity of iron oxide detected. The elemental composition of CNS was studied using the EDS technique. Figure 6(a) shows a bright field TEM image from the performed scanning transmission electron microscope (STEM) mode to run EDS. Figure 5(b-c) shows the element contents (C, Fe, S and O) and distribution in the area. The appearance of C peak with only 6.7 percent indicates low carbon supply during synthesis process, which might lead to low population of CNTs growth. Fe and O peaks were from the catalyst used, while Cu peak were detected from the TEM grid. EDS results also reveal some impurities of S peaks. Sulfir (S) was used during the manufacturing of NR gloves as crosslinking agent to increase the mechanical strength of the products.

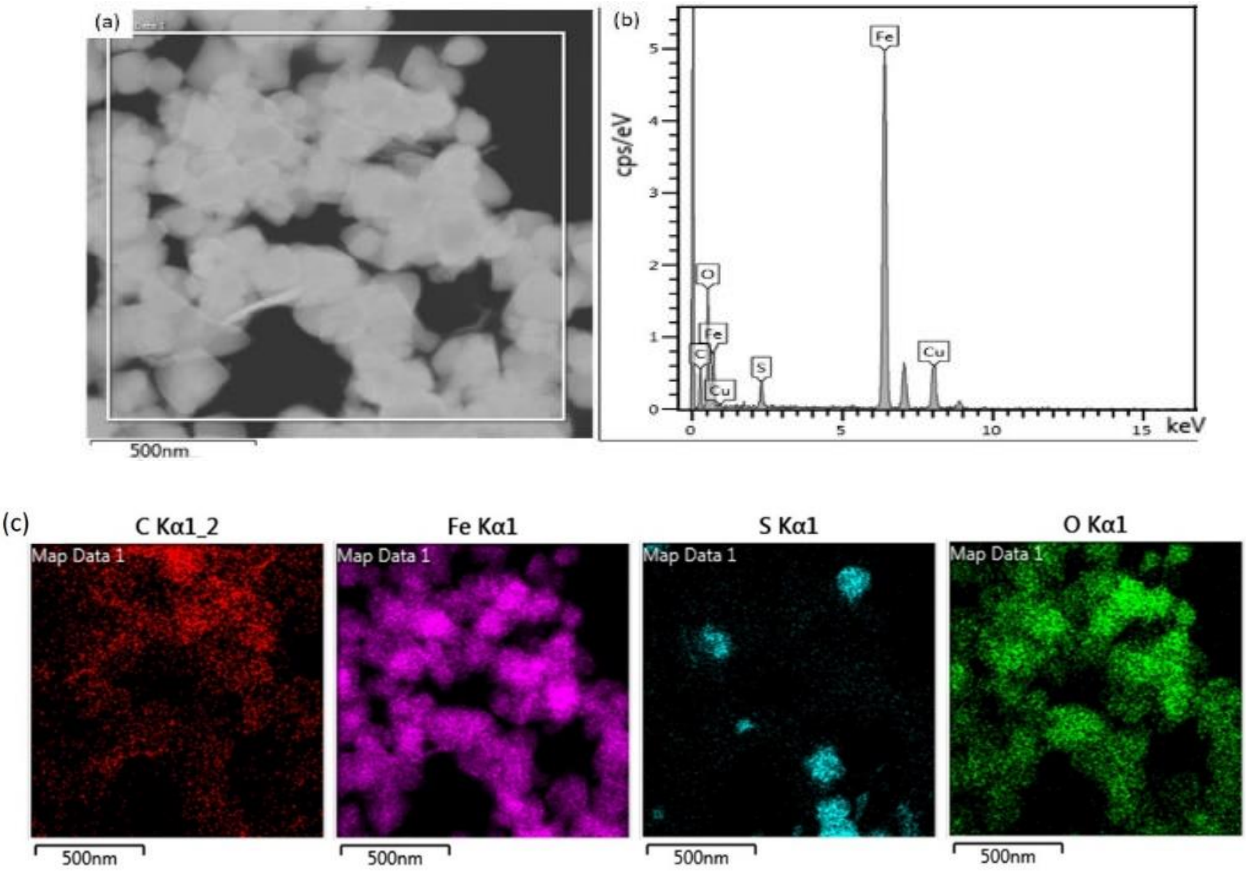

Figure 6. (a) Bright-field Scanning Transmission Electron Microscopy (STEM) image and (b) corresponding EDX spectra (c) EDX elemental maps showing, respectively, the spatial distribution of C, Fe, S and O in the selected area of the CNS.

Conclusion

We have demonstrated that CNS were successfully synthesized using waste latex from natural rubber gloves as carbon source via chemical vapor deposition. The CNS was obtained on iron oxide catalyst as confirmed by atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Energy-dispersive X-ray spectroscopy (EDS) and Raman analysis. It was found that the obtained carbon material existed in the form of nanotubes, fibers and nanocapsules with diameter of 5 - 20 nm. The I_G/I_D value was found to be approximately 0.84, indicating CNS in the samples were not well crystalline and contain defects. HRTEM images and EDS results reveal non-uniform of large catalyst size and impurities of carbon source might lead to less population of grown CNTs. Thus, our findings show that various forms of CNS can be synthesized from waste NR gloves as carbon precursor by CVD.

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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.

Disclosure of Conflict of Interest

The authors have no disclosures to declare

Compliance with Ethical Standards

The work is compliant with ethical standards

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