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Contributed Paper

Candle Flame Synthesis and Electrochemical Behavior of Chain-like Carbon Nano-onions on 304 Stainless Steel

Saifon Kruehong [a], Chaiyaput Kruehong*[a, b], Prinya Chindaprasirt [c] and Apichart Artnaseaw [a]

[a] Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, 123 Friendship Rd., Khon Kaen 40002, Thailand.

[b] Integrated Nanotechnology Research Center (INRC), Faculty of Science, Khon Kaen University, 123 Friendship Rd., Khon Kaen 40002, Thailand.

[c] Sustainable Infrastructure Research and Development Center (SIRDC), Faculty of Engineering, Khon Kaen University, 123 Friendship Rd., Khon Kaen 40002, Thailand.

*Author for correspondence; e-mail: chaikr@kku.ac.th

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ABSTRACT

The feasibility of chain-like carbon nano-onions on 304 stainless steel substrate by candle flame synthesis was described. The carbon nanomaterials were synthesized at 600 °C for 180 seconds on the 1 cm × 0.5 cm 304 stainless steel wafers. SEM and TEM analysis results of carbon nanomaterials showed that it was chain-like carbon nano-onions of 40-70 nm in diameter with graphite structure. The ratio of the G and D band intensity (I_G/ I_D) of Raman analysis was 1.03. In addition, the chain-like carbon nano-onions-coated 304 stainless steel was applied as working electrode in three-electrode system. The electrochemical behavior of chain-like carbon nano-onions was characterized by cathodic polarization in KOH and H_3PO_4 solutions. Electrocatalytic behavior of chain-like carbon nano-onions on oxygen reduction and hydrogen evolution reaction was presented in comparison with uncoated stainless steel wafer.

Keywords: combustion, candle flame, carbon nanotubes, polarization, electrolysis

1. INTRODUCTION

During the past decades, various forms of carbon nanomaterials (e.g. carbon nanotubes, carbon nanosphere, buckminsterfullerence) have received strong interest from researchers due to their remarkable physical and electrical properties [1]. At present, these carbon nanomaterials (CNMs) are widely used as advanced materials in biomedical and energy applications [2-3]. For these reasons, CNMs have attracted huge academic and industrial interests. Today, CNMs are primarily synthesized using chemical vapor deposition (CVD). In this method, the carbon source, such as hydrocarbon and carbon monoxide, is pyrolyzed in the presence of a catalyst

at a suitable temperature for carbon nanotubes (CNTs) formation. However, the development of commercial applications has been rather slow due to their high production cost, complicated production process and difficulty in separation of CNMs from catalyst and supporter. In recent years, the combustion synthesis of CNMs has been reported by several groups [1], [4-5] because it could be a low-cost mass-production alternative to CVD method. However, the catalyst, supporter preparation have not been investigated. Camilli et al. [6] successfully synthesized multiwall carbon nanotubes (MWCNTs) on AISI 316 stainless steel (316 SS) by CVD, without any pretreatment. This is probably due to the presence of catalyst nanoparticles (Fe and Ni) on the surface of 316 SS, as revealed by atomic force microscopy (AFM) analysis [6]. Generally 316 SS has high corrosion resistance due to 2-4% of Mo [7]. However, 316 SS consists of similar percentages of Fe and Ni to those of 304 SS [7]. Based on the literature reviews, we can conclude that Fe and Ni are the main catalysts for the CNM growth [5], [8]. Therefore 304 SS could be a good candidate, in the place of 316 SS, as both the catalyst and supporting material for CNM growth.

This research illustrated a simplified recipe to synthesize chain-like carbon nano-onions (CLCNOs) on 304 SS, by flame synthesis, without the addition of external metal catalysts. The objective of this study was to assess the characteristics of CLCNOs on a 304 SS substrate, using candle as the source of both carbon and energy. The feasibility of graphite structure apparent and electrochemical behavior of CLCNOs was studied. This article presents a new method for synthesizing low-cost CLCNOs on a 304 SS with high oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) in alkaline and acidic solutions.

2. EXPERIMENTAL PROCEDURES

2.1 Measurement of Temperature Distribution of The Candle Flame and Synthesis of CLCNOs

A commercially available candle (Candle Light Pratheep, Thailand) was used as carbon and energy source for the synthesis of CLCNOs. The diameters of the candle and the candlewick were 5 cm and 0.5 cm, respectively, while the length of the candlewick was 1 cm above the candle. The candle was burnt for 1 min until the height of steady flame was 10 cm. At this point, temperature distribution of the candle flame at 1 to 10 cm above the candlewick was measured by thermocouple type K (Fluke model 80PK-

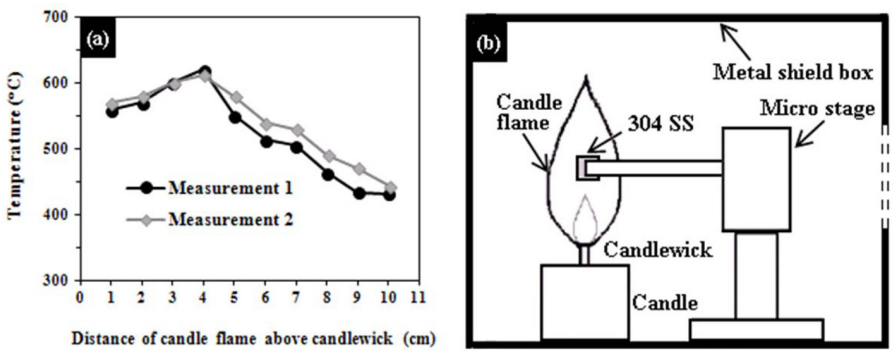

Figure 1. (a) Temperature distribution of candle flame. (b) Schematic of an experimental setup for combustion synthesis of CLCNOs.

22) as in Figure 1a.

A 1 cm × 0.5 cm of as-received 304 SS wafer was used as the substrate as well as the catalyst for the synthesis of CLCNOs. Surface substrate was cleaned and rinsed using ethanol in an ultrasonic bath for 5 min and placed in the steady flame at 600 °C (~3 cm above the candlewick) for 180 sec. Figure 1b shows an experimental setup to synthesize the CLCNOs by combustion of candle.

2.2 Materials Analysis

The surfaces of CLCNOs and stainless steel substrates were studied by scanning electron microscope (SEM, Hitachi S-3400N). The morphology of CLCNOs was characterized by transmission electron microscope (TEM, JEOL JEM-2010). Raman spectrometry (Raman, NT-MDT NTEGRA Spectra) was used to characterize the compositions of CLCNOs. The argon laser with a wavelength of 514.5 nm was used as the excitation source. Spectra were measured in the range of 500-3500 cm^{-1} with the laser power of 5mW. In addition, thermal gravimetric analyzer (TGA, SHIMADZU TGA-50) was used to study the thermal stability of the CLCNOs at a rate of 10°C/min in air.

2.3 Electrochemical Testing

The potentiostat (Gamry Reference 600) was used to study the ORR and HER of the obtained CLCNOs (1.55 mg/cm^2 on 304 SS) in 8 wt% KOH and 8 wt% H_3PO_4 solutions [9]. The electrochemical cell used in this investigation consists of Pt plate of 1 cm^2 as a counter electrode and standard silver-silver chloride electrode (SSE) as a reference electrode. The CLCNO-coated stainless steel of 0.5 cm^2 was applied as the working electrode. Cathodic polarization curves were plotted at a scan rate of 5 mV/s.

3. RESULTS AND DISCUSSION

Figure 2a shows the SEM image and the EDX spectrum of 304 SS surface before combustion synthesis. Fe, Cr, Ni, C and Mn peaks were observed, indicating that 304 SS surface contains Fe and Ni which are well-known catalysts for the synthesis of graphite structures e.g. fullerenes, carbon fiber, and carbon sphere, etc. Therefore, 304 SS can be used as both the substrate and the catalyst for CNMs synthesis and graphite structure observed in CNMs. Figures 2b and 2c show the CNM-coated stainless steel substrate after combustion synthesis at 600°C for 180 sec. The SEM image (Figure 2c) shows higher magnification of CNM-coated stainless steel. It was synthesized in atmosphere at 600°C without being burnt due to graphite

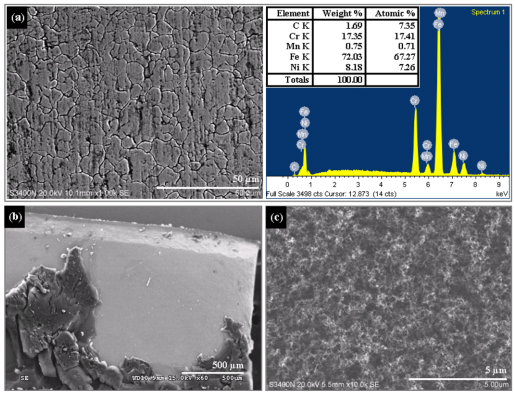

Figure 2. SEM analysis: (a) SEM image and EDX spectra of 304 SS before experiment, (b) and (c) SEM images of CNMs on 304 SS substrate at ×60 and ×10,000 magnifications, respectively.

structure formation.

The TEM images (figures 3a and 3c) show the morphology and the characteristics of the CNMs. The morphology of CNMs was CLCNOs with the diameter of 40-70 nm. The d-spacing of 0.33 nm (figure 3c) was observed in graphite structure. SAED pattern showed a crystalline structure (figure 3b), confirming the growth of CLCNOs. In addition, Raman spectrometry result (figure 3d) showed a first-order D band (1350 cm^{-1}) and a first-order G band (1580 cm^{-1}), indicating a disordered structure and a graphitic structures, respectively. The ratio between the peak intensity of G band and that of D band (I_G/ I_D ratio) was 1.03. The CLCNOs contained structural defect (D band peak) due to the curvature of CLCNOs and the non-uniform structure of graphite. Moreover second-order weak bands also occurred at 2550 cm^{-1} (2D′ band) and 2875 cm^{-1} (D+G band), indicating the presence of parallel graphitic layers of CLCNOs. These results provide a proof of concept that CLCNOs can be grown on 304 SS by combustion synthesis using candle flame technique.

Figure 3e shows the thermal stability of the CLCNOs. This mass reduction can b e used to evaluate the purity of CLCNOs. A three-step thermal degradation process can be observed: the first stage occurred at 400 °C yielded amorphous carbon (5.4% of CNMs); the second stage occurred at 600 °C yielded CLCNOs (91.0% of CNMs); the third stage occurred at 700 °C yielded solid residue from combustion (3.6% of CNMs).

The growth of graphite structure can be described by the interaction between alkane vapors (C_{18}-C_{40}) from candle combustion [10]. The alkane vapors at the surface of catalysts were cracked to the vapors of hydrogen and carbon. The hydrogen vapor can prevented the formation of surface oxide and the oxidation reaction between oxygen and catalysts. Subsequently, the carbon vapor

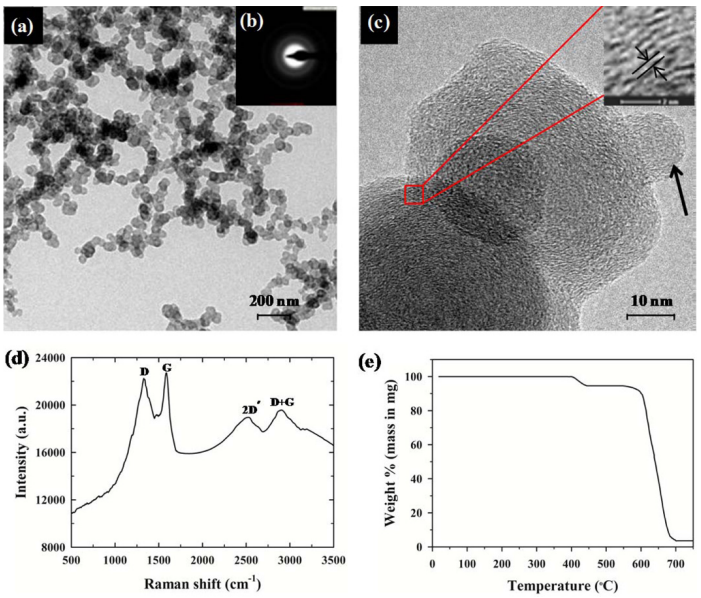

Figure 3. Morphology and characteristics of CLCNOs: (a) TEM image, (b) SAED pattern, (c) High-magnification TEM image, (d) Raman spectra and (e) The thermal stability of the CLCNOs from TGA analyze.

may be deposited on, or dissolved in, these catalysts or surface of CNMs for the growth of graphite structure.

Figure 4 shows schematic diagram for describing a possible growth mechanisms of CLCNOs on 304 SS. During partial oxidation process, a carbon nano-onion (CNO) was initiated through some large catalyst sites (Fe and Ni particles) on the 304 SS surface, which can be described by base growth model (BM) [5]. However, figure 3c reveals that the CLCNOs growth (black arrow) can take place without the presence of catalyst on the surface of a CNO. Lending support to our findings, Dhand et al. [11] were able to synthesize CNOs by flame synthesis from liquefied petroleum gas, without catalyst. Therefore, it is possible that CLCNOs may also grow on a small carbon island on the surface of an established CLCNO. The latter growth mechanism is similar to the Volmer-Weber (VW) growth mode [12] and we hereby propose that it is called the Carbon Particle Model (CPM) of CNMs. In this research, the growth of CLCNOs can be described by combining BM and CPM, in which the initiation of CLCNO growth was described by adsorption of carbon vapor on the catalyst

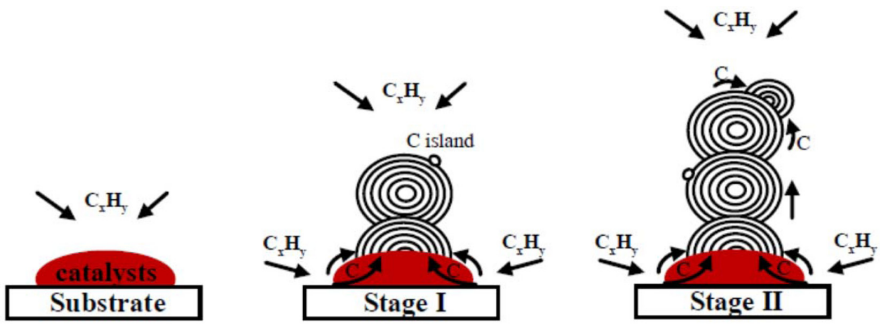

Figure 4. Schematic diagram for describing the growth mechanisms of CLCNOs on 304 SS.

sites in stage I and the formation of each CNO to CLCNOs by either BM or CPM in stage II.

Figures 5a and 5b show cathodic polarization behavior of CLCNO-coated stainless steel compared with uncoated stainless steel cathodes in KOH and H_3PO_4 solutions. The ORR and HER behavior of CLCNOs exhibited higher current density than that of stainless steel cathode in both alkaline and acidic solution. This confirmed that the increase of cathodic reaction behavior was due to the coating of 1.55 mg/cm^2 of CLCNOs on stainless steel substrates. However, due to strong HER in acidic solution, CLCNOs were peeled off during hydrogen evolution. The current density of the coating decreased to the level comparable to that of the stainless steel substrate. It was clear that surface properties of CLCNOs

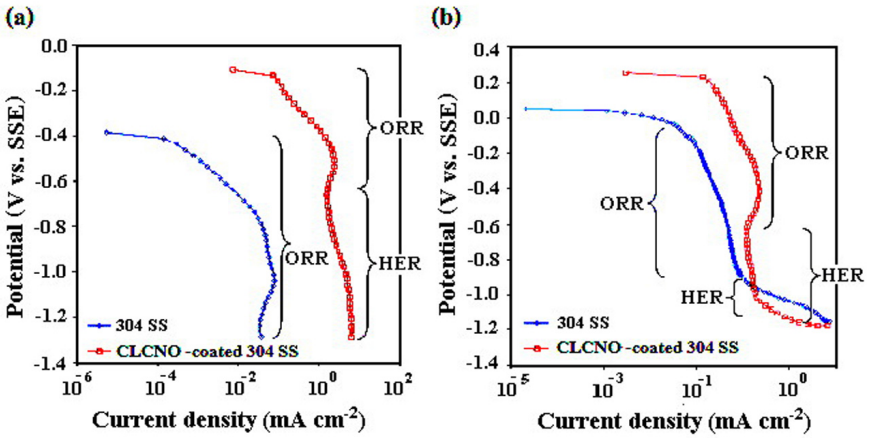

Figure 5. Cathodic polarization behavior of CLCNO-coated stainless steel compared with 304 SS cathodes: (a) in KOH solution and (b) in H_3PO_4 solution.

increased the ORR and HER due to its catalytic behavior in the alkaline and acidic solutions.

4. Conclusion

The 91% CLCNOs can be synthesized by combustion of candle using 304 SS as both substrate and catalyst. The obtained CLCNOs were 40-70 nm in diameter, with the I_G/ I_D ratio of 1.03. Moreover, the coating of CLCNOs can increase the ORR and HER of stainless steel in both alkaline and acidic solutions. It was suggested that their excellent electrocatalytic behavior makes CLCNOs suitable materials for modern energy applications such as fuel cell, electrolysis and battery, in which they can be used as cathode material.

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