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Letter to the Editor

## The formation of a nanocarbon from lignocellulose with a sea anemone appearance

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## ARTICLE INFO

## Article history:

Received 25 September 2012

Accepted 5 December 2012

Available online xxxx

## ABSTRACT

A filamentous carbon nanomaterial having morphology, elemental compositions and growth conditions similar to those of a sea anemone was formed during pyrolysis of lignocellulose in the presence of water and sodium. We call the material “carbon nano-anemones” (CNAs). Well known carbon nano filamentous materials such as carbon nanotubes find extensive applications in electronics, hydrophobic coatings, catalysis and sensor technology. However, they are inert, non-polar, hydrophobic and surface chemical modification is often necessary before use. CNAs, on the other hand, contain oxygen, are reactive, polar and may be suitable, without modification, for applications e.g., catalysis, sensors.

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Increasing energy demands, concerns over environmental issues and depletion of fossil resources are amongst the driving forces to use renewable feedstock to meet the future energy needs [1]. Lignocellulosic biomass is a renewable source for fuels [2]. It can be converted to a bio-crude oil via pyrolysis at atmospheric pressure and temperatures around 500 °C [3]. Currently, there is tremendous interest in developing catalysts to make this conversion efficient and to improve the properties of bio-oil to suit application as feedstock in a conventional oil refinery. Formation of solid carbonaceous material is typical and acceptable during pyrolysis reaction as it helps in improving the energy density of the resulting bio-crude oil. However, these carbonaceous materials are usually in the form of char, a low value by-product material. We have recently shown that sodium modified amorphous silica alumina (Na/ASA) catalyst is promising for the pyrolysis conversion of lignocellulosic biomass (Canadian Pinewood) to bio-crude oil having a higher energy content (24 MJ kg<sup>-1</sup>) than

a non-catalytic thermal process (18 MJ kg<sup>-1</sup>) [4]. During this pyrolysis experiment (450 °C, 1 bar, 20 min), a new type of carbonaceous material having filament-like morphology similar to sea anemones was observed (Fig. 1a and c) (for detailed reaction and catalyst preparation procedures please see Supplementary material). The features of sea anemones are strikingly similar to carbonaceous material observed in the pyrolysis experiment (Fig. 1b and d). For this reason we term them as carbon nano-anemones (CNAs). The anatomy of sea anemones (Fig. 1a and c) contains elongated flexible extensions called tentacles. Carbon nano-anemones have very similar filamentous features (Fig. 1b and d). They have tips at the free end of their structure similar to that observed for sea anemones at the end of their tentacles. Furthermore, similar to sea anemones, CNAs do not have any unique spatial orientation.

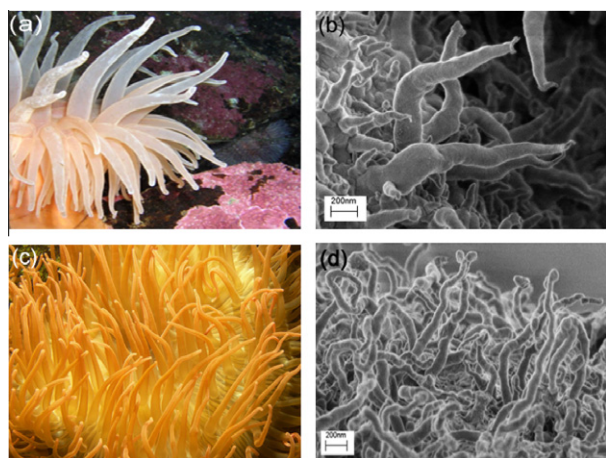
With respect to chemical composition, the tentacles of sea anemones are mainly composed of proteins with H, C, O and

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<http://dx.doi.org/10.1016/j.carbon.2012.12.006>

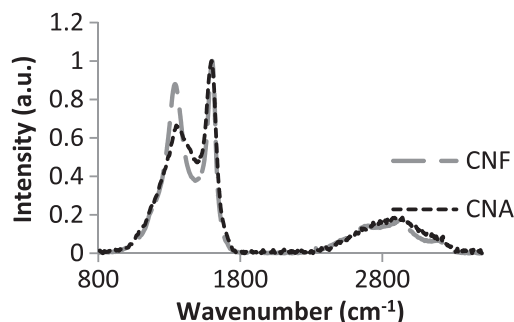


**Fig. 1 – (a and c) Images of sea anemones, (b and d) high resolution SEM pictures of CNAs formed during pyrolysis experiment; image (a) was taken from [www.valdosta.edu](http://www.valdosta.edu), (c) was taken from [www.cepolina.com](http://www.cepolina.com).**

N in their elemental composition [5]. Results from elemental analysis indicated that CNAs are also composed of H, C and O (H, 7.8 wt.%; C, 63.5 wt.%; O, 28.7 wt.%).

Sea anemones are mostly found in shallow levels (atmospheric pressure and temperatures) of saline water. The level of  $\text{Na}^+$  in saline water is higher compared to other minerals (for example: 10800 ppm of  $\text{Na}^+$  vs. 1290 ppm of  $\text{Mg}^{2+}$ ) [6] and therefore it is suggested that the presence of  $\text{Na}^+$  ions is crucial for the growth of sea anemones. Likewise, the growth of CNAs in our experiments depends crucially on the presence of  $\text{Na}^+$  ions in the catalyst. Under identical reaction conditions, CNAs were observed only when  $\text{Na}^+$  was present on the catalyst (Na/ASA vs. ASA catalyst, Fig. 2a and b). The carbon deposit in the absence of  $\text{Na}^+$  was in the form of a thin layer of carbon. Remarkably, other alkali ions such as  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  also did not cause formation of CNAs when they were applied in the same reaction under identical reaction procedure (see [Supplementary material](#) for preparation and reaction procedures).

The morphology of CNAs looks similar to conventional CNFs (Fig. 2b and c). The Raman spectra of CNFs and CNAs also appear to be similar (Fig. 3). The spectra of CNFs consisted of two narrow peaks with maxima at  $1602\text{ cm}^{-1}$  and  $1341\text{ cm}^{-1}$  corresponding to graphite (G band) and disordered graphite (D band) bands, respectively. The broad peak in range of  $2500\text{ cm}^{-1}$  to  $3400\text{ cm}^{-1}$  is assigned to second order



**Fig. 3 – Raman spectrum of CNFs and CNAs.**

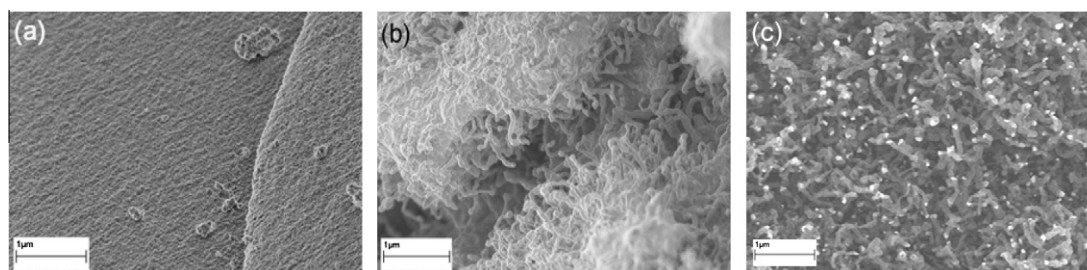
“D” bands, i.e., combinations modes and overtones [7]. Nevertheless, in the Raman spectrum of CNAs the “D” defect band is broader. Looking also at the “G” band for both cases it can be concluded that CNAs also have certain amount of crystallinity but qualitatively different from CNFs.

The difference between CNAs and CNFs emerges clearly in their physical and chemical properties. Carbon nanofibers are composed of graphitic C (97.4 wt.%) and small amount of H (0.4 wt.%) and they grow in the presence of transition metals, i.e., Fe, Co and Ni.

Carbon nano-anemones, on the other hand, have C (63.5 wt.%), H (7.8 wt.%) and O (28.7 wt.%) in their elemental compositions and they form successfully in the presence of  $\text{Na}^+$  and require no transition metals. The absence of transition metals was confirmed by X-ray fluorescence and energy dispersive X-ray analysis.

Based on the temperature programmed oxidation analysis (see [Supplementary information](#) for the method), the oxidation of CNAs starts at  $220\text{ }^\circ\text{C}$  and the whole material are combusted by  $450\text{ }^\circ\text{C}$ . On the other hand, the oxidation of CNFs (prepared at  $450\text{ }^\circ\text{C}$ , using metallic Ni as catalyst and ethylene gas as the source of carbon) starts at around  $460\text{ }^\circ\text{C}$  and they are fully combusted at a much higher temperature of  $800\text{ }^\circ\text{C}$ . Therefore, CNAs are more reactive in oxygen.

Oxygen containing carbon nano filaments, formed during the pyrolysis of lignocellulosic biomass on Na/ASA catalyst resemble sea anemones. Formation of CNAs is an advantage in catalytic pyrolysis of biomass since it is reactive and easy to burn off, thus making the regeneration of the catalyst possible at lower temperatures. Moreover, presence of oxygen makes CNAs reactive and much more flexible for modifications, e.g., polarity, anchoring of chemical groups, etc., and opens scope for technical applications such as in sensors.



**Fig. 2 – High resolution SEM of (a) ASA, (b) Na/ASA after pyrolysis experiments, and (c) CNF.**

This intriguing finding of CNAs open up a new scope in the field of functionalized carbon materials.

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### Acknowledgements

The authors would like to thank L. Lefferts, D.B. Thakur, (University of Twente, Enschede) and F. A. Nikayin (TU Delft, Delft) for useful discussions and M.A. Smithers (University of Twente, Enschede) for his help in SEM imaging.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2012.12.006>.

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