Carbon Nanotubes (CNTs) Produced from Natural Cellulosic Materials

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Summary

In this study we provide evidence that the cellulose microfibril arrangement occuring naturally within plant walls[1] aids in the formation of CNTs when plant fiber is carbonized in a cyclic oxidation process. We demonstrate that nanometer-scale channels are formed early in the cyclic oxidation process because of the differential thermal stability of the carbonaceous residues from cellulose microfibrils and the lignin matrix. This research supports the concept that these channels may act as templates[2] for the formation of CNTs as carbonization proceeds. The use of plant materials in the production of CNTs has the potential to significantly reduce production costs, and it also suggests unique applications for plant fiber incorporation into thermally produced products.

Materials and Methods

We used 6 materials, ranging from plant fibers to purified lignin and cellulose substrates (Table 1). All of the starting materials were heated either:

1) Continuously in air for several hours at ambient pressure; or

2) In a cyclic manner with small amount of air under negative pressure.

All materials were pre-carbonized in air at about 240 ºC.

Determination of the specific thermal schedules for CNT production required 2 years of experimentation.

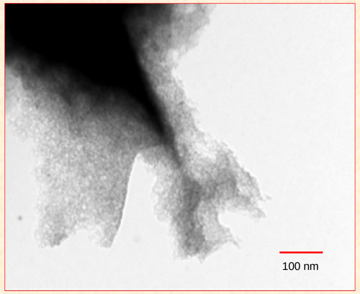
Table 1. Carbon Source Type

Carbon Material	Wood	Bamboo	Lignin	Filter paper	Avicel	α - cellulose
Form /Morphology	Thermo-mechanical pulp (TMP)	Small particles	Fine powder	10 mm wide by 20 mm long strips	20 micron micro-crystalline cellulose	Fine powder

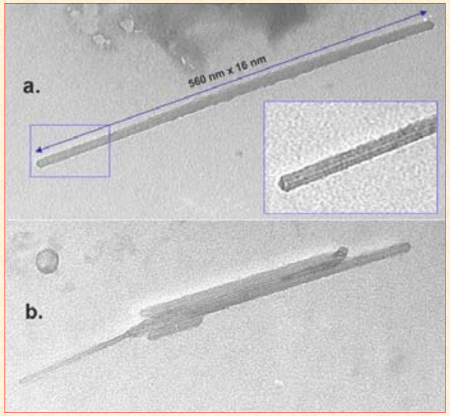
Results

Table 2. Results from Sample Observation under TEM

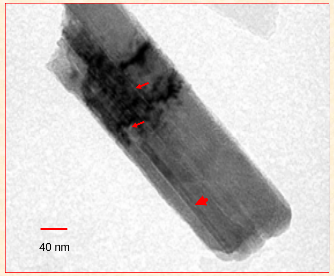
Raw Material	Continuous Heating	Multicyclic Process
TMP/Bamboo	No tubular structures	Carbon containing CNTs
Filter paper	No tubular structures	No carbon remained
Alpha-cellulose	No tubular structures	No tubular structures
Avicel	No tubular structures	No tubular structures



TEM image of carbon containing no tubular structures. This image shows the typical amorphous structure of carbon.

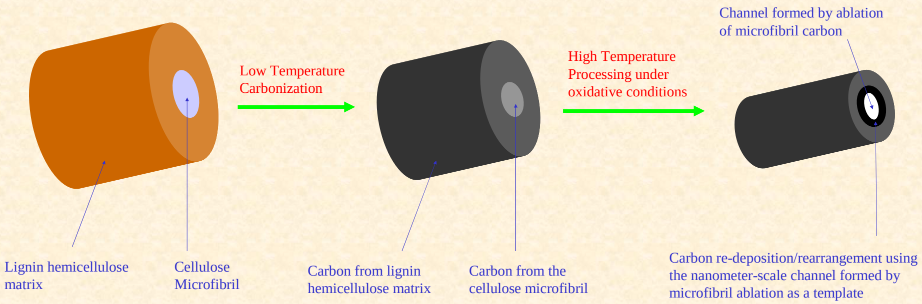


TEM image of CNTs produced from natural cellulosic materials. (a) A typical single CNT: The dimensions indicate that it is a multi-walled CNT (MWNT). (b) An aligned CNT bundle: Samples were obtained after about 35 oxidative carbonization cycles.



TEM image of natural cellulosic materials after two oxidative carbonization cycles. Small arrows: Nanometer-scale channels with diameters range from 5nm to 20 nm, which falls in the dimensional range of microfibrils located within plant cell walls[3]. Large arrow: CNT formation in a 20 nm channel. This is a strong proof that CNT formation is mediated by the nanochannels produced by microfibril ablation.

Proposed Mechanism



Schematic of the formation of CNTs from secondary plant cell walls during oxidative carbonization

Discussion

- The nanometer-scale arrangement of the chemical components in plant cell walls may play a critical role in the formation of CNTs. No tubular structures were formed in purified lignin and cellulose, but only in unmodified plant cell wall material.
- The cyclic carbonization process was effective in the complete ablation of delignified wood fiber (filter paper), which is a good representation of natural cellulose[4].
- The common continuous heating process produced only amorphous carbons.

Conclusions

- CNTs, about 16-20nm in diameter and up to about 600nm long, have been produced from natural cellulosic materials using a multicyclic heating procedure at relatively low temperatures.
- We propose that the formation of the CNTs in this procedure are catalyzed by nanometer-scale channels formed through the ablation of cellulose microfibrils.

References

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Acknowledgements

This research was funded by the Office of Naval Research and the federally funded Wood Utilization Research (WUR) program at the University of Maine.