



## **STRUCTURE AND POROSITY REGULATIONS OF CARBON MATERIALS BY THERMAL-TREATMENT AND AIR OXIDATION**

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### **Introduction**

Carbon materials can be tuned into new forms by different methods like arc-discharge, laser-blazing, plasma treatment, thermal treatment, oxidation and so on [1][2], resulting in the formation of new carbon substances with broadly different structures and properties. Thermal treatment has a long history of improving the graphitic state of carbon, and air oxidation method has been widely used to open the inaccessible pores. With the emergence of variety of novel carbon materials, understanding their structural and property evolution under heat-treatment, and controlling the accessibility of their inside pore-space has significant consequences for designing new carbon materials with required properties.

### **Materials and Methods**

In this work, four kinds of carbon materials, including porous graphene (abbreviated as PG) prepared from reduction and KOH activation of graphene oxide [3], an activated carbon fiber (abbreviated as ACF, Osaka Gas Co. Ltd), a carbon black (abbreviated as CB, Mitsubishi Chemical Co. Ltd) and a single wall carbon nanohorn (abbreviated as CNH, NEC Co. Ltd), are heated at different temperatures up to 3073 K. Their structural evolution are comparatively studied by using N<sub>2</sub> adsorption isotherms (77 K), transmission electron microscopic (TEM), X-ray diffraction (XRD) and Raman spectroscopy.

The oxidation method is employed to open the internal nanospace of above mentioned CNH and a single wall carbon nanotube (abbreviated as CNT, NanoIntegris), and thermal-treatment is employed to close the created nanowindows. The pore-opening and pore-closing procedure are repeatedly conducted to test the reversibility of their porosity.

### **Results and Discussion**

The classic work on the graphitization of carbon by R.E. Franklin [4] indicates that graphitizable carbons have weakly-linked, compact and nearly parallel-oriented carbon crystallites, while non-graphitizable carbons have rigidly-linked carbon crystallites of random orientation. As a typical non-graphitizable carbon, ACF cannot form high crystallinity even been heat-treated at 3073 K. However, PG has a remarkable crystallization process under heat-treatment even if its carbon units have no pre-orientation. The unusual graphitization behavior of PG should be ascribed to its unique microscopic structure of graphene units, i.e., mono- or few layer graphene sheets of large planar size and high flexibility.

CB has parallel-oriented graphene units, which tend to mutually stack with each other under heat-treatment. However, the curvature and defects of graphene layers in thermal-treated CB distinguish their structure from well-defined crystal. CNH show minimum graphitization among all carbons at temperature below 2273 K, but start to graphitize quickly at above temperatures.



This is because the strong carbon bonds connecting individual carbon nanohorns hinder their mutual interaction if the energy is not sufficient.

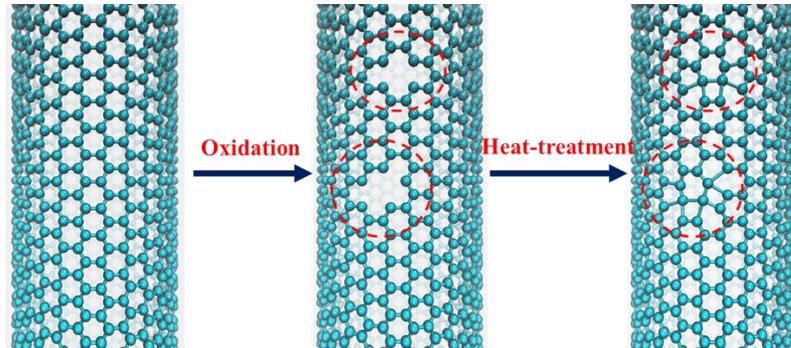


Figure 1. Mechanism of pore open and pore close on CNH or CNT.

Air oxidation can expose the inaccessible nanospace of CNH or CNT by opening nano-windows on their graphene walls. On the other hand, heat-treatment can recombine the carbon atoms surrounding the nano-windows and then close the nano-windows. The porosity of both CNH and CNT don't show significant change after three times opening-closing procedure, suggesting a good porosity reversibility.

## References

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