# Thermal Stability and Reducibility of Surface Oxygen and Nitrogen Functional Groups on Carbon Nanotubes and Their Application in Electro-catalysis

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## Introduction

Because of the inert and hydrophobic nature of carbon nanotubes (CNTs), it is necessary to introduce surface functional groups for their applications. $HNO_3$ treatment is one of the most frequently used methods for the introduction of oxygen-containing functional groups on CNT surfaces [1]. Moreover, nitrogen-containing functional groups can be incorporated in the CNT structure either during growth of the CNTs, or via post-treatment by $NH_3$, $N_2$ plasma, etc. Given the intensive studies on the functionalization methods in recent years, the knowledge on the thermal stability and reducibility of these functional groups is still insufficient. At present, nitrogen-containing CNTs (N-CNTs) receive much attention in electrocatalysis. However, the nature of the active sites on N-CNTs is still not clear.

In this presentation, we introduce a highly effective gas phase method for the oxygen functionalization of CNTs through $HNO_3$ vapor treatment, where more oxygen groups especially –COOH and C=O can be introduced to the CNT surface as compared to the conventional treatment with liquid $HNO_3$ due to much higher treatment temperatures [2]. The thermal stability and reducibility of surface oxygen groups were studied by X-ray photoelectron spectroscopy (XPS) in ultra-high vacuum (UHV) and hydrogen, respectively [3]. The transformation of different groups upon heating was investigated. Furthermore, nitrogen was incorporated into the CNT structure either via pyrolysis of acetonitrile over Co catalyst or via post-treatment by $NH_3$ at different temperatures. The amount and the type of the N-functional groups were identified by high resolution XPS. The N-CNTs were used as non-metal electrocatalysts for oxygen reduction reactions (ORR) for the cathode side of PEM fuel cell. These studies provided insight into the nature of the active sites and the influence of different nitrogen functional groups on the ORR activities.

## Materials and Methods

The $HNO_3$-vapor treatment of CNTs was performed at different temperatures from 125°C to 200°C. The thermal stability of O- and N-containing surface groups on CNTs was investigated by temperature-programmed techniques (TPD and TPR) and temperature-resolved high-resolution XPS. The catalytic activity of N-CNTs towards ORR was studied using rotating disk electrode (RDE) and scanning electrochemical microscopy (SECM) measurements.

## Results and Discussion

The deconvolution of XP C1s and O1s spectra allows the quantitative determination of different oxygen species on CNTs. The evolution of different oxygen-containing functional groups upon heating in UHV and hydrogen was investigated by XPS (Fig. 1). It was found that the decomposition of the carboxylic groups occurs in the lower temperatures range, whereas the phenol, ether, and carbonyl groups are more stable and decompose at higher temperatures. $H_2$ has a marked influence on the thermal stability of the surface functional groups. The functional groups can be removed by direct reduction (carboxyl, phenol, quinone, carbonyl *etc.*), or through destabilization of their anchoring to the carbon surface (anhydride *etc.*) in the presence of $H_2$. A similar study shows that N-groups introduced by post-treatment with $NH_3$ decreased significantly upon heating. In contrast, the N-groups introduced to the CNT structure during growth via pyrolysis of acetonitrile are thermally more stable and show almost no decrease in the total content of nitrogen.

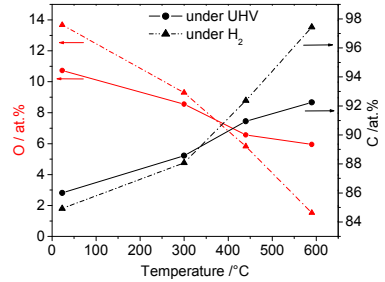


**Figure 1**. Variation of the XPS-derived composition of oxygen-functionalized CNTs after pre-treatment in UHV and $H_2$ at different temperatures.

RDE and SECM studies demonstrated that the incorporation of nitrogen in the CNT structure enhances the activity dramatically as compared to nitrogen free CNTs even in acidic electrolyte medium. In particular, the N-CNTs with a higher amount of pyridinic groups showed a 100 fold increase in the kinetic current, which is comparable to the commercial Pt/C catalyst with a Pt loading of 20 wt% (Fig. 2). This increase in the kinetic current is attributed to the increase in the stability of carbon structure against oxidation and an increase in the basic nature of graphite structure due to incorporation of nitrogen.

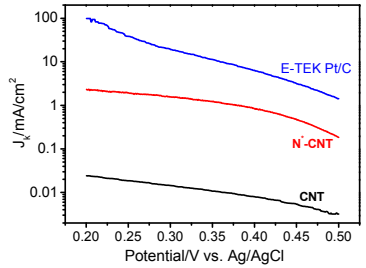


**Figure 2**. Tafel plots for $O_2$ reduction in oxygen saturated 0.5 M $H_2SO_4$ medium under a rotation speed of 900 rpm.

## Significance

The $HNO_3$ vapor treatment is a simple, but highly effective method for the oxygen functionalization of CNTs. The thermal stability studies are of vital importance for the application of CNTs involving high temperature processes such as in catalysis. The application of the N-CNTs for ORR deals with one of the major challenges in fuel cells as well as in chlorine industry.

## References

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