

# MODIFICATION OF CARBON NANOTUBES FOR HETEROGENEOUS CATALYSIS

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## Abstract

Surface modification of carbon nanotubes was performed by functionalization, defect creation, and the growth of secondary filaments with iron as catalysts. X-ray photoelectron spectroscopy, transmission electron microscopy, scanning tunneling microscopy, Raman spectroscopy, nitrogen physisorption, temperature programmed desorption and other techniques were employed to characterize the modified nanotubes. The specific surface area was enhanced and the amount of surface defects was increased after modifications. By tuning the growth conditions, secondary filaments of different dimensions were prepared, leading to three dimensional carbon composites of different morphologies. The modified nanotubes were used as support for palladium nanoparticles deposited from vapor phase. The Pd/C catalysts were tested and found to be very active and stable for the hydrogenation of cyclooctene.

## Introduction

Among the different types of supports used in heterogeneous catalysis carbon nanotubes (CNTs) attract a growing interest due to their specific characteristics including their high purity, excellent conductivity, good mechanical and thermal stability, chemical resistance, and the possibility to control the porosity and surface chemistry. Several methods such as incipient wetness impregnation, ion-exchange, deposition/precipitation, and chemical vapor deposition (CVD) have been used to prepare CNT-supported catalysts. A variety of applications have been investigated with CNT-supported catalysts, including hydrogenation reactions, fuel cell catalysis etc. Recently, carbon has been employed as non-metallic catalysts for various reactions such as oxygen reduction in fuel cells and oxidative dehydrogenation for the synthesis of styrene. The active sites, although not yet clearly established, are believed to be related to surface defects, especially to edge planes.

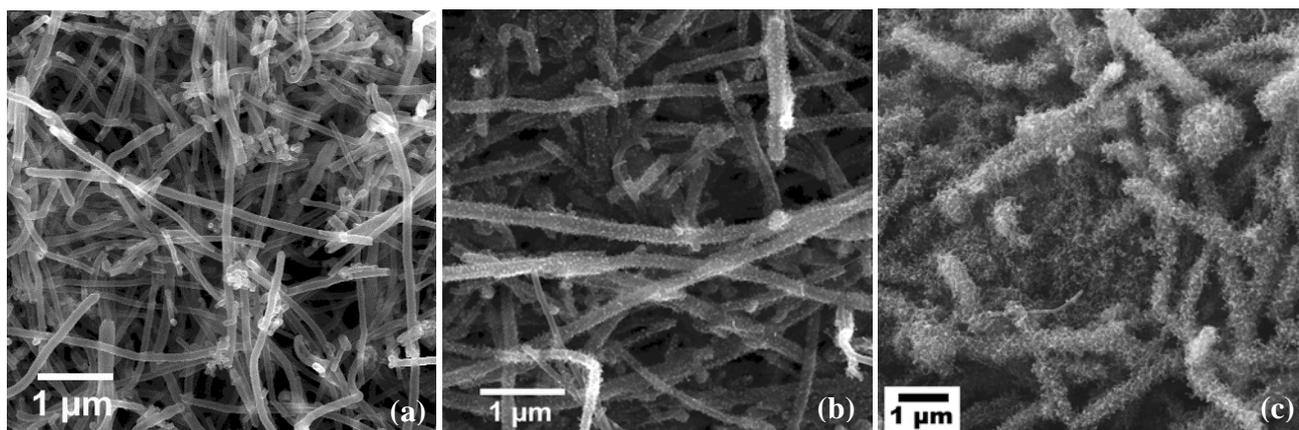
As-grown CNTs are normally covered by a thin layer of polyaromatic hydrocarbons formed during preparation. The polymer coating is inert at room temperature but unstable at elevated temperatures frequently employed for catalytic reactions, thus has to be removed before applying to catalysis. Thermal treatment (pyrolytically stripping), normally in inert gases, is very effective to remove the hydrocarbons, and purified CNTs can thus be obtained. Nevertheless, further treatments are still necessary due to the inertness of the carbon surface. A more active surface is favorable for the deposition of catalytic active metal nanoparticles. Oxidation is among the most intensively studied methods to modify and functionalize the inert carbon surface. The frequently used strong oxidation media include nitric acid, oxygen plasma, supercritical fluids, ozone etc.

Until recently the modification of CNTs is mainly limited to oxidation, followed by side chain extension when necessary. We demonstrate in this report the modification of CNTs by branching and controlled etching.

## Branching of CNTs

CNTs (diameter 100-200 nm, length 30-100  $\mu\text{m}$ ) were employed as support for secondary CNTs. The parent CNTs were first exposed to a 120 W oxygen plasma for 7 min in a rotating barrel. The plasma-treated nanotubes were used as substrate for the CVD of iron oxides in a fixed-bed reactor with ferrocene as iron precursor. Transmission electron microscopy (TEM) studies evidenced the presence of homogeneously distributed particles with diameters of 1-2 nm. More over, X-ray photoelectron spectroscopy (XPS) studies were performed on the Fe/CNT samples. The surface atomic concentrations of both iron and oxygen decreased considerably after the thermal treatment in hydrogen at 700°C, indicating severe sintering of iron nanoparticles before the growth of secondary CNTs. The XPS observations are in agreement with the TEM investigations, which shows that the particle size increased to 5-9 nm after sintering.

Subsequently, secondary CNTs were grown on the parent CNTs from cyclohexane with the iron nanoparticles as catalysts. By controlling the growth time, secondary CNTs of different lengths were obtained. The as-received CNTs were characterized by smooth surface (Figure 1a). Figure 1 (b) and (c) show the SEM images of the secondary CNTs grown on the parent CNTs (CNT/CNT) with growth time of 5 and 30 min, respectively. It can be seen that the secondary CNTs are distributed homogeneously over the surface of the parent CNTs. With increasing growth time, the length of the secondary CNTs increases. The specific surface area of the as-received CNTs is in the range of 20-30  $\text{m}^2 \text{g}^{-1}$ , compared to only 10-20  $\text{m}^2 \text{g}^{-1}$  for the as-grown nanotubes. The increase in specific surface area originates from the pyrolytic stripping applied to remove polyaromatic hydrocarbons. The plasma treatment of the as-received CNTs increased the specific surface area to 83  $\text{m}^2 \text{g}^{-1}$  due to surface roughening. After the growth of the secondary CNTs for 30 min, the specific surface area was found to increase significantly to 205  $\text{m}^2 \text{g}^{-1}$ . It is worth noting that the specific surface area of the carbon composites was determined in the as-grown state. An even higher specific surface area can be expected when the thermal treatment or the plasma treatment are additionally performed.



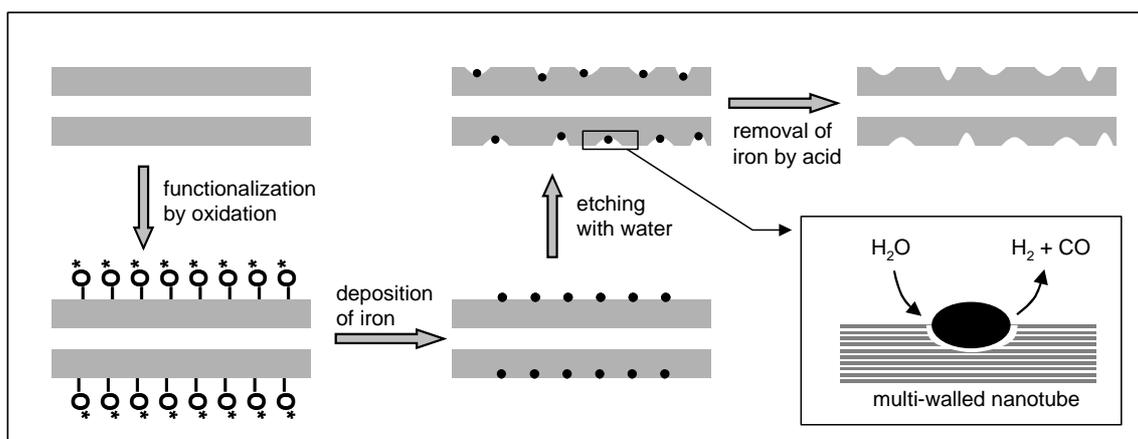
**Figure 1.** SEM images of plasma-treated CNTs (a), and CNT/CNT composites grown for 5 min (b) and 30 min (c) at 700°C from cyclohexane in a mixture of H<sub>2</sub> and He (2:1, total flow rate 37.5 ml min<sup>-1</sup> (STP)).

In Summary, the CNT/CNT nanocomposites were synthesized by exclusively employing gas-phase reactions. The modified parent CNTs exhibit a 3-dimensional structure with an enhanced specific surface area. By further deposition of metal nanoparticles such as palladium, platinum or ruthenium, a unique structured hydrogenation or fuel cell catalyst can be obtained. The tailored composite is therefore of great potential as a structured support for carbon-supported catalysts especially in three-phase reactors and in fuel cells.

### Catalytic etching by H<sub>2</sub>O

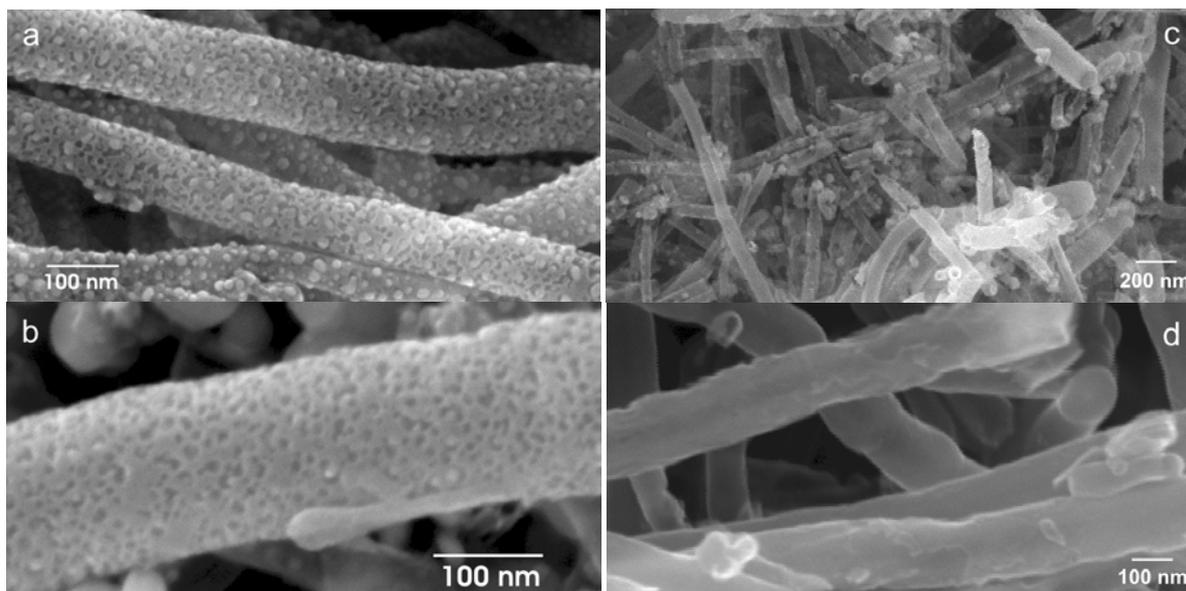
In order to enhance the number of active sites on CNT surface, we developed recently a localized etching route to selectively modify CNTs in a pre-determined manner. The etching, based on the catalytic steam gasification of carbon, occurs only at the interface between the nanotubes and the iron nanoparticles. Different etching patterns can be obtained by tailoring the size and the spatial distribution of the iron particles. The areal density of surface defects such as edge planes, which are believed to be the main active centers in catalysis, is significantly enhanced. Only water and iron as readily available chemicals are employed in this eco-friendly process producing hydrogen and carbon monoxide as major components of synthesis gas.

The novel etching method of CNTs is summarized in Scheme 1. The nanotubes are first functionalized by oxidation to introduce oxygen-containing groups, which are necessary for the anchoring of foreign species. Iron is subsequently deposited on the nanotubes either from the gas phase (CVD) or by impregnation. Following the post-deposition treatment of the iron nanoparticles, etching is performed at elevated temperatures by introducing water vapor. The walls of the nanotubes are selectively destructed as a result of the etching. Finally, the iron nanoparticles are removed by washing with diluted acid, and nanotubes with etching patterns are obtained.



**Scheme 1.** Schematic illustration of the four major steps involved in the etching process.

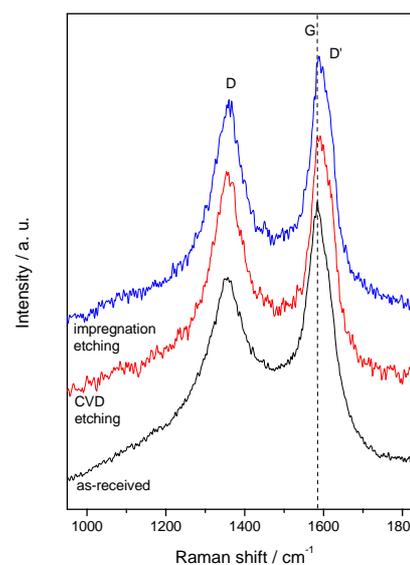
The morphology of the CNTs resulting from the etching using CVD-deposited iron particles is shown in Figures 2 (a) and (b). The iron oxide nanoparticles are embedded in the walls of the nanotubes after etching (Figure 2a). The diameter of the particles is in the range from 5 to 12 nm. Restricted movement of iron particles obviously occurred during the reaction resulting in etching pits larger than the particle size. The area beyond the mobility radius of the iron particles was not affected by the etching. The hemispherical carving patterns are more clearly visible after the removal of the iron oxide particles by washing with acid (Figure 2b). Small pores are selectively created in the initially smooth surface of the as-received nanotubes. In case of impregnation, the resulting iron particles are larger compared to CVD (Figure 2c). Etching for 1 h leads to the partial destruction of the walls of the nanotubes. In contrast to the CVD samples, the etching patterns are frequently observed in the form of steps, although etching pits and holes can also be observed (Figure 2d). Obviously, etching catalyzed by larger iron particles results in large-area etching patterns, other than tiny pits.



**Figure 2.** SEM images of the CNTs after etching by water. (a) 5 wt% Fe by CVD, with iron nanoparticles; (b) 5 wt% Fe by CVD, after dissolving the iron nanoparticles in acid; (c) 5 wt% Fe by impregnation, with iron nanoparticles; (d) 5 wt% Fe by impregnation, after dissolving the iron nanoparticles in acid.

High resolution TEM investigations clearly demonstrate the destruction of the wall of the nanotubes. The graphene sheets of the wall were obviously destroyed one after another. As a result of the etching, new edge planes were created. The newly exposed surfaces are obviously very rich in defects such as steps, kinks, vacancies, and adatoms. The increase of the number of surface defects is also detected by Raman spectroscopy. It is known that highly ordered pyrolytic graphite is characterized by the so-called G-band at  $\sim 1580\text{ cm}^{-1}$ , whereas microcrystalline graphite shows additional bands around  $1350$  and  $1620\text{ cm}^{-1}$ , called D and D' bands respectively, due to the presence of lattice defects and the loss of the long range in-plane symmetry. There is strong evidence that the loss of hexagonal symmetry due to the formation of edge planes is associated with the D lines. It can be seen in Figure 3 that the intensity ratio of the D band to the G band increased significantly due to etching, for both the CVD and the impregnated samples, indicating a considerable increase in the areal density of surface defects. In addition, the contribution of the D' band appearing as shoulder of the G band to higher wavenumbers was increased by etching, which is an additional clear indication for more surface defects.

As compared to the original CNTs, after etching more oxygen- and nitrogen-containing functional groups can be introduced to the surface of the nanotubes by a treatment with nitric acid, as demonstrated by XPS quantitative measurements. Furthermore, the functional groups created



**Figure 3.** Raman spectra of as-received and etched CNTs.

on etched CNTs are thermally more stable, which is very important since many catalytic applications of CNTs involve high-temperature processes.

In summary, a localized etching method based on catalytic steam gasification of carbon was developed to modify carbon nanotubes in a pre-determined manner. The etching, occurring only at the interface between the iron nanoparticles and the nanotubes, created different etching patterns depending on the iron catalyst by means of an eco-friendly, low-cost process using water vapor. Both the surface roughness and the number of surface defects such as edge planes were significantly enhanced. The controlled etching is expected to extend the applicability of CNTs, because it was found to be beneficial for the creation of functional groups. Furthermore, fiber-matrix interactions in composites are expected to be enhanced for etched CNTs, and sintering of supported metal particles anchored in etching pits should be less severe.

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