



# Encapsulation of copper and zinc oxide nanoparticles inside small diameter carbon nanotubes



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## ABSTRACT

Copper and zinc oxide nanoparticles have been reproducibly deposited into carbon nanotubes (CNT) of 6–7 nm internal diameter via simple impregnation techniques with different metal salts followed by thermal decomposition of the precursors and reduction in H<sub>2</sub> in case of Cu. Oxygen functionalization via a gas-phase method involving thermal shocks was a critical step while traditional functionalization with nitric acid resulted in failures. Intra-CNT location of CuO particles could be proven by STEM images, and was examined by TEM for materials prepared by various routes. It was found that Cu and Zn oxide nanoparticles could be deposited throughout the whole interior CNT space. The filling capacity depended on the preparation conditions, on conditions of subsequent precursor decomposition, and on the inner diameter of the CNTs. After the reduction of the CuO nanoparticles, XRD, XAFS, and N<sub>2</sub>O reactive frontal chromatography indicated a bimodal particle size distribution due to the presence of agglomerates outside the CNTs. To enhance selectivity for endohedral location, a washing step with HNO<sub>3</sub> with the inner CNT space blocked by xylene was applied to selectively remove aggregates in the outer space. Based on the best procedures for introduction of CuO and ZnO, a bimetallic CuZnO@CNT sample was prepared via a consecutive preparation route.

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## 1. Introduction

Since the upsurge of research on carbon nanotubes (CNTs) following Iijima's report on their formation during fullerene synthesis [1], these materials have been also extensively studied as catalysts or catalyst supports. This effort has recently created evidence on a dependence of catalytic and redox properties of catalytic components on their location. Thus, Fe<sub>2</sub>O<sub>3</sub> turned out to be reduced at lower temperatures when deposited in the interior space than on the outside of small CNTs [2], catalytic activities of Fe (in Fischer–Tropsch synthesis [3]) or Rh (for the formation of ethanol from synthesis gas [4]) within the hollows were superior to those exhibited by the same metals when deposited onto the CNTs. This was ascribed to an “electronic confinement effect”, which causes a shift in the  $\pi$ -electron density to occur when the inner diameter (i.d.) decreases below 10 nm [5,6]. These results have raised the interest in filling CNTs of very small i.d. with metals or metal oxides also among catalytic scientists.

The deposition of metal oxide nanoparticles within CNTs was described already a decade ago [7]. Most studies undertaken since

then employ impregnation techniques supported by ultra sound, performed with cut nanotubes to facilitate the filling of the inner space by the solutions employed [8]. Such impregnation can be combined with selective washing steps to remove species simultaneously deposited on the exterior surfaces [9]. Impregnation with different solvents favorably interacting with the interior or the (functionalized) exterior CNT surfaces has been shown to result in selective deposition of the particles in the interior or on the outside [10]. Choice of ligands for the precursors to be deposited [11] or chemical modification of exterior or interior surfaces [12] are strategies for increasing deposition selectivity on the basis of molecular recognition. Volatile compounds may be introduced into CNTs via the gas phase [13], and even the use of supercritical CO<sub>2</sub> has already been reported [14]. For CNTs with >15 nm i.d., there is a rich literature on deposition of various compounds into the interior space (e.g. [15–17]). Filling of CNTs becomes, however, more difficult with smaller diameters [18]. Deposition of oxide clusters into CNTs of <10 nm i.d. has succeeded so far only by ultra-sound supported impregnation [8].

In the following, we report the deposition of copper and zinc oxide particles in the interior space of CNTs with 3–5 nm nominal i.d. This effort was driven by the interest to create model catalysts for the investigation of Cu–ZnO interactions in industrial methanol synthesis catalysts. While there are numerous reports on the

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introduction of Fe, Co, Rh, Ru, or Pd into CNTs of similar sizes [2,8,10,19–21], literature on the deposition of Cu and Zn oxide is scarce. Problems may be envisaged for Cu due to decreasing interactions between the graphene surface and transition metal atoms at increasing number of d-electrons [22,23]. While this may interfere with the stabilization of small Cu metal particles, already the synthesis of Cu oxide nanoparticles is complicated by the existence of highly mobile hydroxo nitrate intermediates, which have to be carefully avoided to obtain satisfactory dispersions (e.g., in nanoporous SiO<sub>2</sub> [24]). There has been a report on successful deposition of Cu oxide particles into CNTs of 4–10 nm nominal i.d. [25], however, the route did not provide the desired results with some of our materials and may therefore be not general. Literature on modification of CNTs with ZnO appears to be limited to deposition on the exterior surface by now [26].

We will now describe new, reproducible routes for the selective encapsulation of copper and zinc oxide nanoparticles in the channels of CNTs with small diameters. The particles were studied by electron microscopy (STEM, TEM), XRD, and XAFS. In the case of copper, the reduction behavior of the oxide species was investigated by temperature-programmed reduction (TPR). After reduction, the size of the metal particles was assessed by N<sub>2</sub>O reactive frontal chromatography (RFC), by XAFS, and by XRD.

## 2. Experimental

### 2.1. Material synthesis

Raw CNTs (CheapTubes Inc., Brattleboro, U. S. A., nominal i.d. 3–5 nm, length 10–50 μm) were functionalized by thermal stress following a procedure adapted from literature [27]. By moving a quartz tube into and out of a tubular furnace, the raw material was instantaneously heated to 873 K in a flow of 150 ml/min dry air and after 10 min rapidly cooled to room temperature where it was kept for 12 min. This sequence was repeated twice. The procedure removes the caps of the nanotubes as well as amorphous carbon and it is able to shorten long CNTs [27]. It is very severe, further repetition leads to complete loss of the CNTs. CNTs functionalized by this route will be denoted as O-CNT. From these, N-CNTs were made by treatment in 10% NH<sub>3</sub>/He at 673 K according to a procedure outlined in [28] (for details see [29]).

Alternatively, CNTs were also functionalized by refluxing in concentrated HNO<sub>3</sub> (68%) for 14 h, subsequent washing and drying (→CNT-A).

For some experiments, short commercial CNTs were used (CheapTubes Inc., nominal i.d. 3–5 nm, length 0.5–2 μm). In addition, wide CNTs (Pyrograf, Applied Science, i.d. around 50 nm) were employed for a reference preparation. Both CNT materials were functionalized via the gas-phase route, the wide CNTs will be designated as CNT-Py.

The following route based on O-CNTs will be described as the “standard route” for deposition of CuO nanoparticles in the CNT interior: O-CNTs were added into a solution of Cu(NO<sub>3</sub>)<sub>2</sub> in tetrahydrofuran (THF) (0.0096 mol/l) followed by tip sonication for 1 h while cooling with a water bath. “Tip sonication” denotes a procedure where the ultrasonic power is directly introduced to the solution by a Sonotrode (UIS250LK tip sonicator, Hielscher Ultraschall-Technologie, maximum power 100 W). Subsequently, the solvent was evaporated slowly under ambient conditions prior to drying the solid at 323 K for 10 h. For precursor decomposition, the sample was heated to 523 K in He at a rate of 5 K/min and the temperature was kept for 2 h. The decomposition temperature was specified on the basis of a thermogravimetric measurement (see Fig. S1, supporting information). The lowest possible temperature was chosen because further temperature increase was found to

result in significant CuO particle sintering and clustering [29]. The material produced via this route will be denoted as CuO<sub>ts</sub>/O-CNT. A copper loading of 10 wt.% was targeted in the preparations.

Parameters of the preparation, e.g. Cu source, solvent, type of CNT functionalization, were varied for optimization purposes. In addition, a number of preparation techniques described in literature for the deposition of other metals species in CNTs [3,5,20] were adopted for Cu by changing the metal precursor to copper nitrate. This work is described in detail in [29], only conclusions thereof will be given below.

A washing procedure to remove agglomerates outside the CNTs, the formation of which could not be avoided even in the best preparations, was developed following ideas outlined in [5,9,10]. First, the inner channels of the calcined sample were blocked with xylene (1.25 g per 50 mg sample) by subjecting the slurry of CNTs in xylene to an ultrasonic bath for 4 h. The solid was filtered off, added to concentrated HNO<sub>3</sub> (68 wt.%) and stirred for 30 min. Finally, the sample was filtered off again, washed with water and calcined under the same conditions as before.

ZnO nanoparticles were encapsulated in the CNT interior by impregnating O-CNTs with a solution of zinc citrate (Zn<sub>3</sub>C<sub>12</sub>-H<sub>10</sub>O<sub>14</sub> \* 3 H<sub>2</sub>O) in aqueous ammonia (0.126 mol/l) to incipient wetness. The resulting solid was dried at 323 K for 10 h before it was heated in He to 623 K at a rate of 5 K/min where the temperature was kept for 2 h. It should be noted that this decomposition temperature, which was again chosen on the basis of TG data (Fig. S1) is higher than that employed for CuO/CNT preparations. The sample with a nominal zinc loading of 10 wt% will be labeled as ZnO<sub>iwi</sub>/O-CNT. An alternative preparation paralleled the one described above for copper: the functionalized CNTs were impregnated under tip sonication with a solution of Zn(NO<sub>3</sub>)<sub>2</sub> in THF (0.0094 mol/l). After impregnation, the same drying and thermal treatment at 623 K was applied.

Based on the previously described routes for the preparation of monometallic samples, a consecutive preparation route was developed for bimetallic samples. First, zinc oxide nano particles were encapsulated in the CNT interior following the route for ZnO<sub>iwi</sub>/O-CNT before the sample was impregnated with copper as described for CuO<sub>ts</sub>/O-CNT. After both impregnations, the washing step was applied. For comparison, Cu and Zn were also introduced into CNT-Py. Due to the large diameter facilitating liquid impregnation, a simultaneous route was employed here: copper and zinc nitrate were dissolved in THF and impregnated under tip sonication.

### 2.2. Characterization

Properties of the CNT supports were studied by nitrogen physisorption and by XPS. BET surface areas and pore volumes were determined with a modified Autosorb 1C instrument (Quantachrome) after outgassing the samples at 523 K in He. XPS spectra were measured with an ultrahigh vacuum setup equipped with a high-resolution Gammadata-Scienta SES 2002 analyzer using monochromatized Al K $\alpha$  as incident radiation. C 1s, O 1s and N 1s were integrated over Shirley-type backgrounds with the Casa-XPS software, for calculation of atomic compositions, the sensitivity factors provided by this software were used.

Elemental analysis was made by atomic absorption spectroscopy. Samples were melted in sodium peroxide and then dissolved in aqueous hydrochloric acid. Afterwards the atomic absorption was measured with a Varian SpectraAA 220 spectrometer.

Transmission electron microscopy (TEM) images were obtained on a Hitachi H-7500 instrument operated at an accelerating voltage of 100 kV. The samples were dispersed in ethanol under ultrasonication and placed onto a carbon film supported over a copper

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