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► **To cite this version:**

Marie-Claude Schouler, Fadel Chamssedine, Daniel Claves. Intercalated Carbon Nanotubes as a Template for the Preparation of Supported Heteroatomic Nanoparticles. *Journal of Nanoscience and Nanotechnology*, 2011, 11, pp.2287-2291. 10.1166/jnn.2010.3556 . hal-04051436

HAL Id: hal-04051436

<https://uca.hal.science/hal-04051436>

Submitted on 30 May 2023

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Intercalated carbon nanotubes as a template for the preparation of supported heteroatomic nanoparticles

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Received: 26 March 2010. Revised/Accepted: 04 May 2010.

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Abstract: Chemistry in confined conditions is explored at the level of the interlayer space of multiwall carbon nanotubes. Starting from preliminary intercalated tubes, a ligand exchange reaction has been successfully conducted within the former Van der Waals gap, resulting in a final dispersion of heteroatomic particles, around 2 nm large and nearly homogeneous in size, on the outer surface of the tubes. Intercalated tubular carbon architectures thus prove to be interesting templates for a bottom-up preparation of chemically complex supported nanoparticles, with potential activities for versatile applications.

Keywords: Nanotubes; Intercalation; Nanoparticles; Quantum dots; Fluorides

1. INTRODUCTION:

Nanoparticles take part in a continuously extending field of future potential applications of which quantum information processing, sensing nano-devices or biomedical progress constitute only a brief outline of the subject. Most of the time, easy handling of such nanosized objects implicitly requires that the latter be associated with an adequate macroscopic support. In this context, carbon nanotubes have already proven to be practical supporting matrices and methods to obtain nanoparticles deposited on their surface keep on receiving a great deal of interest. Still recently, developments in the field ¹⁻⁵ have essentially focused on depositing noble metals under the form of homoatomic nanocrystals which, overall, are rather easily obtained over a few tens of nanometers range. Yet, heteroatomicity may appear highly desirable to "nano" chemists, in view of finely tailoring the properties of such nano-structured hybrid systems, which adds considerable difficulty to the synthesis route, especially if a narrow final size distribution is expected.

We herein initiate an elegant general chemical strategy affording *in situ* growth of chemically complex supported nanoparticles, by starting from intercalated multiwall carbon nanotubes (MWNTs) as precursors. Owing to their graphite-like multilayer constitution, MWNTs are *de facto* more prone than their single-walled homologues to undergo intercalation reactions. Although the latter topic has been somewhat left on the fringe of research on carbon nanotubes, the occupation of the interlayer space of MWNTs with electron donors or more scarcely, with electron acceptors,⁶ has proven possible. In parallel, it can be anticipated that almost any acceptor species intercalated into a carbon host-lattice remains highly reactive, given that the prerequisite for hole-doping such a medium is a strong initial oxidizing character. Therefore, the underlying principle that arises is that p-type doped MWNTs should easily afford a secondary chemical reaction, confined within the limits of their curved interlayer space. Intercalated MWNTs might thus be expected to constitute macromolecular architectures propitious to the preparation of different categories of hybrid materials, with the advantage of the pristine carbon framework as a supporting medium offering strong mechanical resistance, large specific area, intrinsic conductivity... The process developed here yields excellent results in regard to the preparation of supported, tiny heteroatomic nanoparticles, with a narrow size distribution.

2. RESULTS AND DISCUSSION:

Exploitation of the above-described concept has been undertaken as follows. As for graphite,⁷⁻¹⁰ transition metal halides are prototypes of acceptors that can form intercalation compounds with MWNTs, under specific conditions.¹¹⁻¹⁴ Tungsten hexafluoride has then been here chosen as the initial dopant, in reason of its earlier tested ability to readily intercalate into MWNTs.¹⁴ Furthermore, many fluorides are known to be able to evolve toward oxides or oxyfluorides upon ligand exchange. An efficient and mild conversion process, whose origin lies in the affinity of fluorine for silicon, can be obtained through substitution from the hexamethyl-disiloxane (HMDSO) molecule, for instance.¹⁵

Therefore, the latter reaction should constitute an excellent test of the synthetic approach imagined. Note that no particular property is searched here, the study being limited to a very first illustration of the potency offered by intercalated MWNTs in terms of building up functional nanostructures and to the extent to which chemical composition, sizing effects or morphology can be tuned.

Purified MWNTs, catalytically grown from the Boudouard reaction near 500 °C, as reported by Pinheiro et al. ^{16,17}, have been used. The average number of sidewalls observed by transmission electron microscopy (TEM) is in the vicinity of ten for most tubes, in compliance with the estimation deduced from the FWHM of their main XRD reflection, for which the finite-size effect contribution to the global profile is largely prominent. The distribution of interlayer spacing is centered on 0.346 nm. The initial choice of the nanotubes characteristics is dictated by the fact that the efficiency of intercalation was found ^{6,13} to be enhanced when tubes contain a high rate of walls disruptions, which necessitates their synthesis process to be conducted at low temperature.

A sample of WF₆-intercalated MWNTs has then been subsequently prepared upon exposure of the preliminary activated pristine tubes to vapors of the gaseous fluoride, according to a procedure described in more details in the experimental section. Accommodation of the fluoride into the tubular carbon matrix has remained quantitatively low and the average nominal composition of the reaction product, determined by weight uptake, corresponds to a stoichiometric ratio W/C \approx 0.015. The associated diffraction data (fig. 1), collected in the transmission mode in a sealed glass capillary, appear not much modified in regard to the overall profile observed for the raw carbon material. They exhibit essentially the initial graphite-like main line at 25.8° arising from some MWNTs sections which remain unaffected by intercalation. Yet, the diffraction pattern of the intercalated precursor thus obtained also shows the emergence of discrete new Bragg reflections on the low angle side of the former most salient peak, which support the efficiency of the intercalation process. The poor resolution of these additional features is usual and simply bears witness to very short coherence lengths within the intercalated

domains formed and to an intercalation phenomenon essentially limited to the outermost carbon shells, as described in earlier studies.^{13,14} The later size-broadening effect, adding to excessive peak overlap in the region of the main signal arising from the unreacted carbon sections, usually makes it difficult to address without uncertainty the proper structural characteristics of such intercalated domains, since a precise determination of each angular position turns out to be somewhat hazardous. Nevertheless, those roughly defined X-ray signatures basically reflect the perturbation induced in the initial stacking of the carbon shells upon reaction with the gaseous fluoride. Therefore, they consist of (00*l*)-like features,¹⁴ owing to the quasi-lamellar character of the intercalated domains from which they arise. Hence, by considering the previously identified separation between carbon sheets within a tube $d_0 = 0.346$ nm and a standard thickness $e = 0.5$ nm referenced for fluoride intercalants, the expression of the repeat distance along the stacking direction is $I_c = n \cdot d_0 + e$, in which n represents a stage number. Considering now that $l = I_c/d_{00l}$ and that the highest intensity peak for a stage n lamellar intercalation compound has (00*l*= $n+1$) Miller indices, it follows that a stage number of 4 would here suit best the presence of the broad hump and non-zero intensity over the $2\theta \approx 14^\circ$ and $23-24^\circ$ angular zones, respectively.

A tentative mild F/O substitution has then been subsequently carried out through immersion of the intercalated precursor in 4-5 mL of HMDSO for 2 days and at 100 °C, in a closed ampoule. Once substitution completed, the final product could be recovered after evaporation of the excess of HMDSO and its characterization has been carried out using TEM. A JEM-2010 instrument operating at 200 kV and coupled with a CCD camera has been used for observations. Digital images were visualized and recorded using the Gatan DigitalMicrograph™ software. The final product has been directly spread on the grid. In spite of the trouble in bringing images into focus, which arises from the incorrect disposal of tubes in the plane of reference induced by the preparation method, respecting this procedure happens to be essential, given the observations that follow. The usual method that consists in depositing a drop of

a suspension of a product in alcohol has then been preferably avoided, owing to the risk of upsetting the nanotexture upon sonication.

Micrographs of the nanostructured hybrid material thus synthesized are presented on figure 1. It can be seen that the outer surface of most tubes is decorated with nanoparticles (fig. 1a-c). Their adherence to the carbon template turns out to be limited, owing to the absence of active binding sites necessary for anchoring them. Consequently, many of these tiny rounded particles can also be observed directly on the grid (fig. 1d), which allows to distinguish more clearly their rather homogeneous size distribution. The mean diameter is found to be around 2 nm, i.e. typical of the one of quantum dots, no outer size seeming to exceed 3 nm. The effectiveness of the thermodynamically favorable F/O exchange desired could not be directly checked by EDX, owing to the incompatibility between the particles and probe sizes, nor by electron diffraction, which only revealed rings originating from the carbon shells stacking. This highly likely stems from the low relative abundance of particles in comparison with carbon and from the quite small particles size which should result in very diffuse spots. The nature of the nanoparticles formed can then be indicated by a Fourier transform analysis of interplanar separations, using the Gatan software, from some particles lying on the grid and presenting rather net lattice fringes (fig. 1e). As a matter of fact, the distances thus determined comply with those referenced within the tungsten oxyfluoride series $WO_{3-x}F_{2x}$ ($x = 0$ to 2), the WOF_4 phase offering the best correspondence, though a strict homogeneity in composition over all particles can not be ascertained. A partial O/F substitution is well supported by a complementary thermogravimetric analysis of the O-substituted sample which shows a departure of volatile species, whereas the presence of the trioxide form would yield a refractory phase instead.

The provisional mechanism of the overall process is schematically decomposed in figure 2 and should involve as first steps: i) the co-insertion of the HMDSO molecule between the carbon shells, which brings reagents in contact and ii) the subsequent ligand exchange reaction between co-

intercalants of immediate vicinity. This exchange reaction seems manifestly followed by expulsion of the reaction product out of the host-lattice, according to our TEM observations. This is further confirmed by the quenching of any Bragg reflection relevant to intercalation after O-substitution. The phenomenon stems from the fact that $\text{WO}_{3-x}\text{F}_{2x}$ species possesses a strong trend to polymerization, as illustrated by their solid state properties,¹⁸ which therefore results in the formation of clusters instead of maintaining individual intercalated entities. In their final aggregate state, the latter are then largely oversized with respect to the initial separation between the carbon layers of the supporting carbon matrix, causing their expulsion. This is probably accompanied by partial exfoliation of the outermost part of the carbon network where intercalation and substitution took place. Occasionally, some of these clusters seem still embedded in the carbon matrix (fig. 1c), forming so-called “inclusion compounds”. Alternatively, it might also be suggested that at least some particles may form from part of the fluoride reagent not initially intercalated, but simply condensed on the external surface of the tubes. The presence of condensation products following the preparation of intercalated MWNTs had indeed been previously detected in one of our earlier work.¹³ However, no XRD signal from such non-intercalated traces is visible here, so that the above described mechanism should be correct or certainly dominant. The details revealed on figure 1-c also clearly tip the scales in favor of a reaction initially confined between the carbon shells.

At last, the reason why the clusters size remains limited is essentially related to the initial texture of the intercalated precursor. Indeed, since the intercalated reactive zones consist of small and separated domains,¹¹⁻¹⁴ the exchange reaction remains localized, i.e. quantitatively limited, which prevents the final particles from growing too large or agglomerating. The quite moderate temperature used here further plays a part in avoiding coalescence between some neighboring clusters. A high initial stage number, by contributing to keep away the layers of intercalants might also participate in the restriction of the final particle size. Though checking this assertion would require heavier

investigations, it may represent a controllable parameter in the search for a means of tuning the size of nanocrystals produced according to the present procedure.

3. CONCLUDING REMARKS:

Nanoparticles supported on carbon nanotubes are being paid special attention, largely owing to the intrinsic properties of the supporting carbon frame, which might effectively conjugate with the size reduction-induced properties expected from the particles themselves. In this framework, our approach undoubtedly shows that intercalated MWNTs can be interesting precursors for chemical and size control in the course of a bottom-up preparation of such hybrid systems. Considering the extent to which MWNTs mimic the overall chemistry of graphite and regarding the plethora of Lewis acids-based intercalation reactions known for the latter,⁷⁻¹⁰ it is clear that the present innovative synthesis mode offers plenty of scope for developments in the preparation of more or less sophisticated supported nanoclusters with potential activities for versatile applications.

4. EXPERIMENTAL DETAILS

MWNTs were prepared via a catalytic method involving the disproportionation of carbon monoxide (Boudouard reaction) over MgO-supported Co catalyst particles, at 510 °C. A subsequent purification process was then required in order to remove the former catalyst particles and support. A two-steps method was applied, involving a preliminary oxidative treatment in air at 450 °C for 20 minutes, intended to the opening of the initially end-capped tubes. The former operation also constitutes the activation step of tubes in view of their intercalation, by contributing to the removal of amorphous carbon deposits all along the tube axis, which obstruct paths from which the diffusion of guest-species into the carbon lattice can occur. The temperature used was optimized by TGA and

corresponds to the starting point of decomposition in air of our tubes. Once freed from their initial protective carbon coating, Co catalyst particles located at the tips could then be removed by acid washing with concentrated HCl (oxoacids should be preferably avoided so as to prevent the formation of oxygenated surface groups). Though TEM observations confirmed the global efficiency of the purification technique, the persistence of small amplitude signals arising from a minor amount of residual Co particles remains visible in XRD. Yet, a complementary TGA up to 600 °C in air, during which only carbon is consumed, shows that the relative amount of carbon represents more than 99 % in weight after purification, and in regard to the present study, such Co traces are not bothersome.

The present experimental conditions for the preparation of the MWNTs-intercalated precursor reproduce those previously used for the intercalation of the same fluoride into graphite. Hence, tungsten hexafluoride was prepared in a first reactor connected to F₂/N₂ gas flows, by direct reaction of a pure fluorine atmosphere with the metal heated at 300 °C, so as to obtain an efficient formation of the fluoride. In order to increase the rate of the intercalation reaction desired, and owing to the high volatility of WF₆, the batch of purified MWNTs was put in a secondary reactor, cooled at -20 °C with a salt-ice bath and connected to the main reactor, for the gaseous fluoride formed to condense on the inner side of this container. The system was then isolated and placed at room temperature during 24 hours. After reaction, the WF₆-MWNTs material was stored and handled in a glove box due to its air sensitivity.

Fig. 1

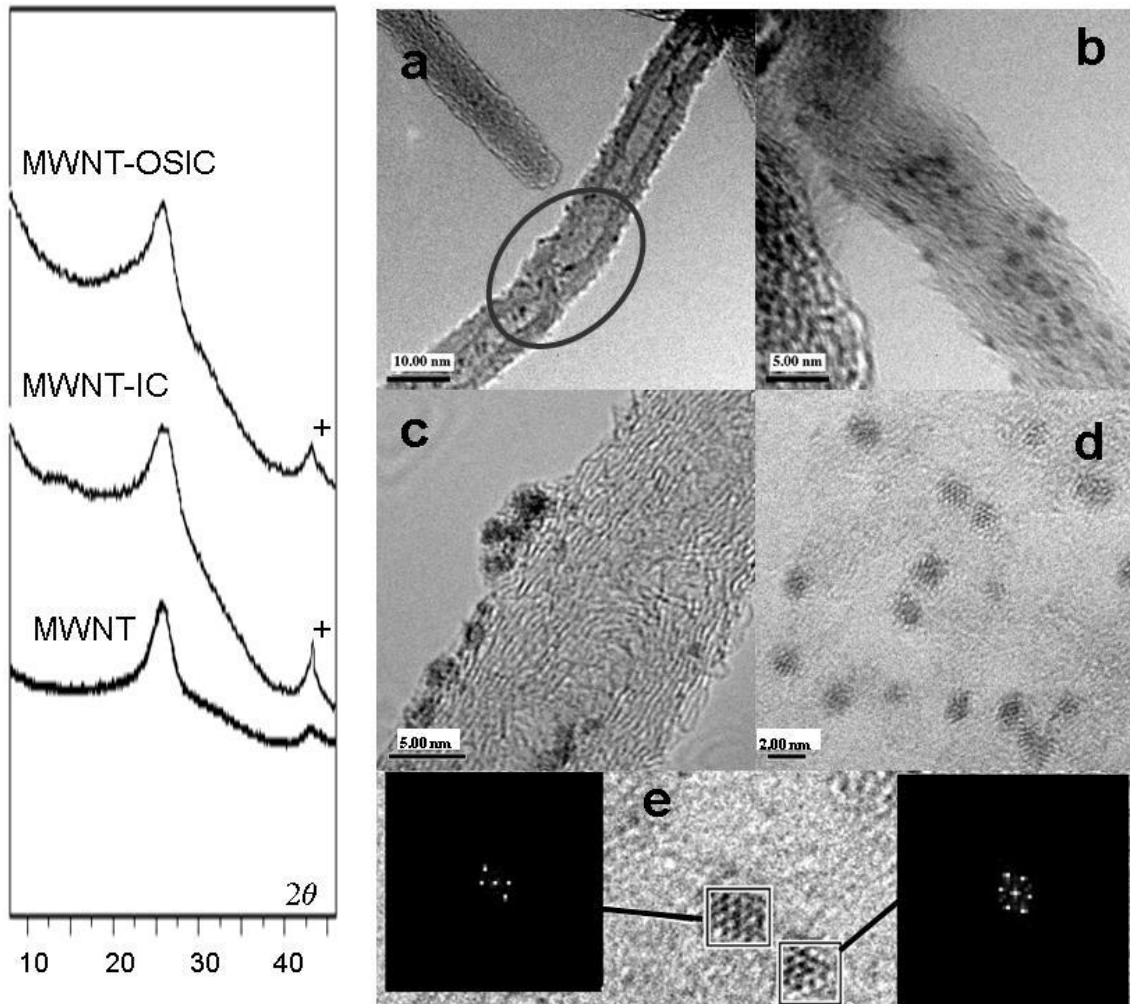


Fig. 2

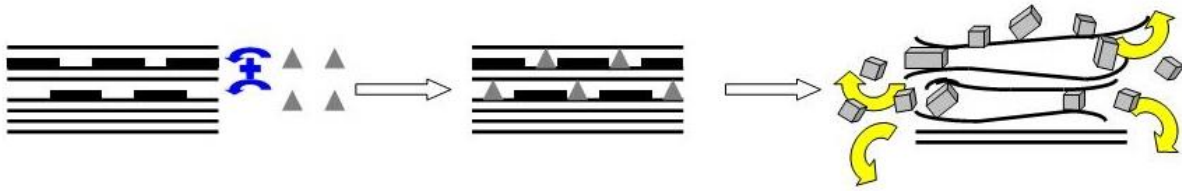


Figure captions

Fig. 1: (Left) XRD patterns ($K_{\alpha 1}$ Cu) of the pristine MWNTs, WF_6 -MWNT intercalation compound (IC) and final O-substituted product (OSIC-MWNT). (Right) TEM micrographs after the O/F substitution showing (a and b) MWNTs decorated with nanoparticles (c) Clusters embedded in the carbon matrix (d) Nanoparticles on the grid and (e) Examples of pairs of spots resulting from FFT analysis and from which d-spacing values can be refined.

(+ denote signals arising from residual cobalt catalyst particles)

Fig. 2: Schematic view illustrating the mechanistic scheme of the nanoparticles formation: (from left to right) i) co-intercalation ii) reaction in the interlayer space iii) clustering-induced volume change at the level of the confined reaction product, followed by expulsion and partial surface destruction of the host-lattice.

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