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## Carbon nanotubes and catalysis: the many facets of a successful marriage

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Carbon nanotubes have emerged as unique carbon allotropes that bear very interesting prospects in catalysis. Their use is mostly related to that of supports for inorganic metal catalysts, including molecular catalysts, metal nanoparticles, metal oxides or even more complex hierarchical hybrids. However, several reports have shown that they can intriguingly act as metal-free catalysts, with performance often superior to that of other carbon materials, in particular when *ad hoc* organic functional groups are attached prior to catalytic screening. The range of catalytic reactions is quite wide, and it includes standard organic synthesis, electrocatalysis, photocatalysis as well as other important industrial processes. In the last few years, the energy sector has acquired a dominant role as one of the most sought-after fields of application, given its ever-increasing importance in society.

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### Introduction

The year 1991 marks a milestone in the timeline of what will be in the following years named “nanotechnology revolution”, as the official discovery of carbon nanotubes (CNTs) has been witnessed.<sup>1</sup> The advent of these new carbon allotropes, together with the gradual unravelling of their fascinating structural and electronic properties, created a sensation among scientists, who foresaw a bright future for these carbon nanomaterials in several scientific areas, such as photovoltaics,<sup>2–4</sup> integrated circuits,<sup>5</sup> biosensors,<sup>6</sup> and nanomedicine.<sup>7–9</sup>

Catalysis is one field of application where the employment of carbon nanotubes has been enjoying a big momentum. Many reports have unequivocally demonstrated that the function of CNTs may be either that of true catalysts or (more often) that of catalyst supports. When used as direct catalysts, CNTs generally require modification with some organic functional groups, introduced through a range of synthetic procedures, although pristine CNTs have also been reported to be catalytically active in several reactions. When used as supports, CNTs are hybridized with transition metal species, which are the truly active species.

Despite an enormous number of papers reporting the use of CNTs in catalysis (but also in various other applicative fields), it can be stated that, as of this time, CNTs have yet to completely fulfill the great promises that they held. In some cases, CNT-based catalysts represent just structurally exotic

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*nanostructure-based catalysts for energy applications.*

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alternatives to better established nanomaterials. Several reasons account for this fact, and at present, great efforts are being channelled towards tackling those most important limitations which delay the full breakthrough of CNTs in real life devices or applications.

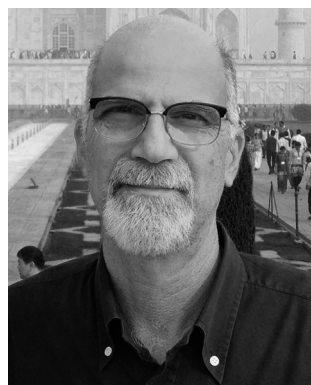
One key aspect to consider is the high cost/performance ratio of CNTs as compared to that of standard heterogeneous catalysts or catalyst supports such as metal oxides (silica, alumina, *etc.*) or amorphous carbon (AC). Current preparative methods such as arc discharge or laser vaporization that afford good quality CNTs are only fit for small-scale syntheses.<sup>10</sup> However, chemical vapor deposition (CVD) is rapidly developing as a reliable method for larger-scale reactions at reduced cost, this being essential for a real impact in industry.<sup>11</sup> In addition, other protocols using CO as carbon feed are being optimized and they allow medium-to-large-scale production.<sup>12,13</sup>

A distinction has to be made between single-walled (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The former seem to bear greater potential in many fields, including catalysis, but in contrast to MWCNTs, the CVD method is not a viable process for these materials from an economic point of view. Moreover, as SWCNTs are subdivided into three types according to their helicity (armchair, zigzag and chiral), and given that chirality affects their electronic properties, it is highly desirable to control the synthesis in order to have one single type of SWCNT, which is still an unsolved issue. These aspects have further hindered the application of SWCNTs, and most studies have focused on MWCNTs.

Another limitation is the batch variance. It turns out that the optimum control of CNT synthesis, particularly for large-

scale synthesis, to produce homogeneous materials is still not definite, and reproducibility can sometimes compromise the report on catalytic performance. The lack of precise control for perfectly homogeneous CNTs also leads to a change in the CNT characteristics at the nanoscale level. Although current synthetic methods guarantee a more uniform structural and functional behavior than that of AC, there is still room for much improvement. Because the preparation of CNTs normally makes use of metal catalysts for nanotube growth, discrepancies at times arise in terms of metal content of the final materials. This is an important feature to take into account, often neglected in catalysis reports. Especially for virtually metal-free direct CNT catalysts, accurate evaluation of the potential residual metal is demanded, as even ppm fractions of metals can alter catalytic performance, thus tainting the results. Albeit less strict, confirmation of the complete removal, or at least purification towards consistently low levels, of residual metals becomes essential for reproducibility issues also for CNT hybrid and nanocomposite systems, where CNTs mainly act as supports.

Because of the extensive research on CNTs, the remedies to these deficiencies are looming, and like never before, the correct answers seem to be reachable, eventually propelling CNTs as instrumental materials in catalyst formulation at the industrial level. In this perspective article, we critically describe the most recent or more established trends in the utilization of CNTs as catalysts or catalytic supports. We analyze the key aspects determining the potential success or failure of CNT-based systems for a wide range of catalytic applications, particularly their implementation at the industrial level.



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## Metal-free catalysts

Carbon nanotubes, both SWCNTs and MWCNTs, have drawn interest in their use as metal-free catalysts. It is often stated that the use of pristine CNTs (p-CNTs) would be advantageous for those processes requiring electron transfer steps, as the electronic properties of these CNTs are preserved and can be fully exploited. Hence, efforts have been made to try to implement catalytic processes with as-produced (or just purified) CNTs (p-CNTs), although the number of reports is comparatively much smaller than that for modified carbon nanotubes. One of the most critical problems associated with the use of p-CNTs is their high level of aggregation through extended  $\pi$ - $\pi$  stacking, therefore resulting in more difficult liquid-phase manipulation.<sup>14-16</sup> Moreover, for many reactions, the as-introduced organic functional groups play a more direct role in catalysis, often behaving as the active sites. Nevertheless, some success in catalysis with p-CNTs has been achieved.

### Reactions catalysed by metal-free p-CNTs

**Oxidation reactions.** Oxidative dehydrogenation reactions (ODH) appear to be amongst the relatively most established reactions using p-CNT catalysts. In a pioneering study by Schlögl, the use of carbon nanotubes in the ODH of ethylbenzene to styrene was compared *versus* the activity of graphite and soot, and the superiority of CNTs was confirmed by the 37% higher specific yield of styrene.<sup>17</sup> However, despite the nanotubes not undergoing any specific functionalization, the mechanism suggested that oxygen functionalities were involved, so in strict terms, these catalysts should be regarded as oxidized CNTs (o-CNTs, Fig. 1). The authors also carried out some mechanistic studies, discovering that the nature of the active sites is actually not dependent on the  $sp^2$  hybridization of the graphenic framework, but rather on the robustness of the CNT scaffold.<sup>18</sup> This is somehow surprising, given the often invoked electronic properties of CNTs, and such finding should prompt us to avoid common prejudices on CNTs catalytic behavior. In a subsequent study, the successful ODH of 1-butene to butadiene was also achieved. This time, the activity was discussed in terms of the oxygen functional groups introduced into the MWCNT sidewalls during the catalytic reaction, in particular quinone/hydroxyl functional group redox couple being the truly active site.<sup>19</sup>

These and other related reports not only evidence a promising role of p-CNTs in the styrene industry, but also pave the way for similar processes in the production of other chemicals of industrial interest. Indeed, few other reactions have been investigated.

The extended polyaromatic framework of p-CNTs was exploited in the oxidation of ethylbenzene to acetophenone, where  $\pi$ - $\pi$  interactions between the intermediate radical species and the CNT framework were proposed to be the key feature. As a comparison, the introduction of organic functionalities such as COOH into CNTs did not result in any

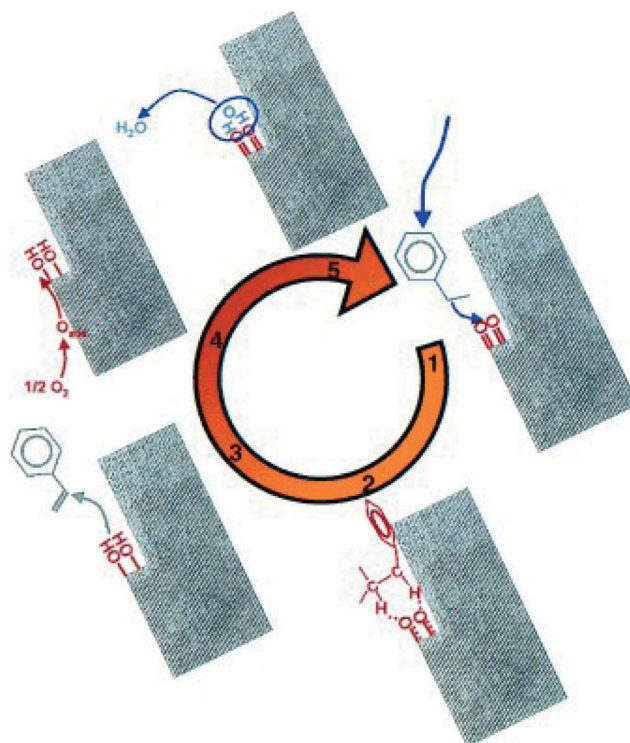


Fig. 1 Mechanism of the catalytic oxidative dehydrogenation (ODH) over carbon nanofilaments: (1) adsorption of ethylbenzene, (2) dehydrogenation at basic centers, (3) desorption of styrene, (4) adsorption of oxygen and reaction with OH groups, and (5) desorption of water. Reprinted with permission from ref. 17. Copyright © 2001 Wiley-VCH.

improvement in the catalytic activity, but on the contrary, had an adverse effect.<sup>20</sup> As one last very recent example, oxidative desulfurization of a model diesel fuel by molecular  $O_2$  was shown to be catalytically activated by several different batches of raw CNTs.<sup>21</sup>

**Electrocatalytic reactions.** The unaltered electronic properties of p-CNTs are in theory very attractive for electrocatalytic reactions, where good conductivity of metallic SWCNTs or MWCNTs can be advantageous to electrode assembly. Very recently, a notable report by Unwin *et al.* revealed that the prejudice on the poor electrocatalytic behavior of p-CNTs remains debatable. By adopting a multi-probe platform based on scanning electrochemical cell microscopy (SECCM), the authors noted an activity of metallic SWCNTs as high as that of standard gold electrocatalysts towards  $O_2$  reduction (ORR). In particular, the activity was enhanced at strained sites formed during oxidation treatment by oxygen plasma etching.<sup>22</sup> p-MWCNTs have been also used as catalysts at the counter electrode for applications in dye-sensitized solar cells (DSCs), and the authors attributed their activity to an increase in the fill factor of DSCs.<sup>23</sup>

### Doping and purity of CNT catalysts

An important possibility arises from doping with, in particular, nitrogen and boron, which allows fine-tuning of the

electronic properties.<sup>24</sup> Notably, pyrolysis of iron(II) phthalocyanine in the presence of  $\text{NH}_3$  vapour and subsequent removal of residual Fe afforded vertically aligned N-doped CNTs which could be used in electrocatalytic ORR with performance superior to that of a commercially available platinum-based electrode.<sup>25</sup> In another comparative study, N-doped MWCNTs and p-MWCNTs both display good activity towards ORR, with the former proceeding through an efficient four-electron process under alkaline conditions and the latter through a two-electron process (Fig. 2).<sup>26</sup>

Other than electrode materials, N-doped CNTs can also perform standard liquid-phase organic catalysis. For example, N-doped CNTs were successfully used in the aerobic oxidation of cyclohexane to adipic acid and its precursors cyclohexanol/cyclohexanone.<sup>27</sup> On the other hand, boron oxide modification of CNTs led to the assembly of a catalyst with remarkable activity and selectivity for the ODH of propane.<sup>28</sup>

One issue that is sometimes neglected, in particular when reporting p-CNT catalysts, is their actual level of purity. The most typical protocols for CNT production rely on the use of metal catalysts such as Fe, Ni and Co that can remain entrapped at relatively high levels. Therefore, eventual detection *via* characterization techniques such as XPS, EDX or TGA is imperative to rule out any possible intervention of the metal in the catalytic reaction. Unfortunately, several literature reports lack a rigorous characterization study and the reported activity of p-MWCNTs is undermined by a significant degree of uncertainty.

### Covalent modification of CNTs and its role in catalysis

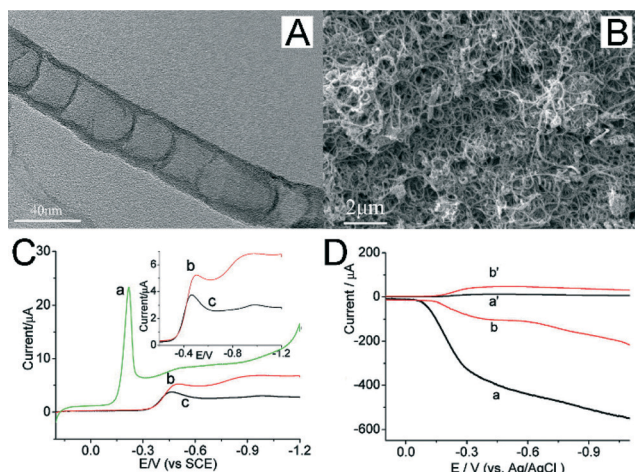
Despite the above notable examples, it appears that a common prerequisite for the employment of CNTs as direct

(metal-free) catalysts involves some kind of chemical modification. Covalent attachment of appropriate chemical entities is a good strategy to improve dispersibility in liquid media by disruption of the  $\text{sp}^2$  system and lowering of the van der Waals forces responsible for bundling.<sup>29–31</sup> Moreover, the as-introduced functional groups may play a key role in the specific catalysis.

Oxidation is the most employed technique in pre-modification of CNTs, which has the dual function of introducing a range of functionalities such as carboxyls, hydroxyls, and epoxides while simultaneously purifying the carbon materials with the residual metallic catalysts remained entrapped during the production step.<sup>32</sup> According to the oxidative protocol, a different distribution of oxygenated groups is introduced, as well as a different distribution of defects. An important improvement for the utilization of o-CNTs would be to precisely control the distribution of various oxygenated groups, or even better to selectively attach single functionalities. Compared with pristine ones, o-CNTs showed great opportunities for ODH. In particular, given the higher resistance to oxidation as compared to amorphous carbon, the ODH of lighter hydrocarbons, where the energy of the C–H bond to be activated is typically in the range of 410–420  $\text{kJ mol}^{-1}$ , becomes a feasible process. In a famous report, CNTs oxidized by simple reflux in  $\text{HNO}_3$  exhibited high activity towards the ODH of very poorly reactive butane.<sup>33</sup>

Different oxidized CNTs displayed clear differences in electrocatalytic hydrogen peroxide reduction and oxidation, a fact related to the diverse structures of o-CNTs, in particular the lengths and widths, obtained after the specific oxidation protocol.<sup>34</sup> Protocols based on reaction with ozone represent interesting alternatives to the common strong acid treatment. In a recent study, each oxygenated functional group (including COOH, OH, and lactones) formed after ozone treatment was correlated with the activity towards ORR and agar conversion, and it was demonstrated that carboxylic acid moieties are actually the essential functional groups for these two catalytic reactions.<sup>35</sup> Similarly, carboxylic acid groups were found to be responsible for the high activity of o-MWCNTs towards the wet air oxidation of phenol, which was completely removed after only 1 hour of reaction time.<sup>36</sup>

Oxidation is not the sole available technique to modify CNTs. In reality, research on organic covalent functionalization has much progressed in the last ten years and as of today, it is possible to design CNTs bearing specific functional groups that exhibit well-defined catalytic behaviors. Access to these functionalized CNTs (f-CNTs) is not necessarily complicated and quite often relies on one-step procedures. A simple  $\text{H}_2\text{SO}_4$  treatment, for example, produced sulfonated MWCNTs which turned out to be active catalysts for the production of biodiesel from cheap feedstock such as oleic acid.<sup>37</sup> Multi-step reaction schemes are required in other cases such as the assembly of amine-functionalized CNTs, which were proven to be suitable for the ring-opening polymerization of *l*-proline *N*-carboxy anhydride (LP-NCA,



**Fig. 2** TEM (A) and SEM (B) images of N-doped CNTs (NCNTs). (C) LSV for the ORR at (a) NCNT/GC, (b) MWCNT/GC and (c) bare GC electrodes recorded in an air-saturated 0.1 M KOH solution at room temperature. Scan rate: 100  $\text{mV s}^{-1}$ . (D) Steady-state voltammograms of NCNTs (curve a and a') and MWCNTs (curve b and b') at a rotating ring-disk electrode in an air-saturated 0.1 M KOH electrolyte. Reprinted with permission from ref. 26. Copyright © 2010 American Chemical Society.

Fig. 3). In this case, however, the f-MWCNTs only acted as radical initiators, and the polymers remained grafted onto the CNT surface.<sup>38</sup>

### Considerations for using CNTs in metal-free catalysis

From the above examples, the versatility and competitiveness of p-, o- and f-CNTs as metal-free catalysts become evident. We believe that there is still much room for incorporation of CNTs into other catalytic processes, particularly where AC is currently employed. The cost difference is still an obstacle, but CNTs have already shown advantages over AC, such as more favourable mesoporosity as compared to the microporosity of AC that allows more facile diffusion of the reactants to the catalytic sites. Moreover, with well-controlled synthesis of CNTs, it is possible to have a more defined distribution of defects that is not possible in naturally occurring AC, which can be instrumental to the selectivity of the catalytic reaction. While the intrinsic superiority of CNTs *versus* AC can be assessed, replacement of metal-based catalysts with nanostructured carbon is a prospect of even higher remarkability.

ODH is a classic example of a successful organic transformation, but it is not unrealistic to realize more sophisticated transformations based on carbon backbone rearrangements, new C–C or C–X (X = heteroatom) bond formation, driven inter- or intra-molecular nucleophilic/electrophilic attack, *etc.*, where the use of appropriately treated CNT catalysts could be implemented.

One more hurdle that needs to be overcome is the large-scale production of CNTs. Currently, economically sustainable methods for the production of large quantities of CNTs are available but generally lead to materials of inadequate purity, while more refined techniques afford materials with high purity but on a much lower scale.

The usually advantageous use of f-CNTs over p-CNTs is counter-balanced by a partial loss of the outstanding electronic properties of the carbon materials, following the degree of disruption of the polyaromatic framework after covalent modification. A classic alternative is to use a non-

covalent approach, where the functional groups are attached by means of CH– $\pi$  or  $\pi$ – $\pi$  stacking and van der Waals forces. These non-covalent molecules can help disperse the CNTs in liquid media while leaving the polyaromatic framework unaltered and can be in principle used as catalytic sites. However, desorption of the molecules during reaction and consequent rapid loss of activity pose a big limitation, and therefore this route has been much less investigated for catalytic applications. Moreover, covalent modification has been associated with a decrease in the toxicity of CNTs, whereas pristine materials are considered to cause much more pronounced adverse health effects.<sup>39,40</sup>

## Hybrids and nanocomposites

A more common form of utilization of CNTs in catalysis is based on their integration with inorganic phases. The resulting materials are called composites or hybrids, depending on whether the inorganic and organic phases are dispersed into each other, thus obtaining a combination of the properties of the two components (composite), or the two phases are interfaced in such a manner that a material with totally new properties not necessarily related to those of the two original components is obtained (hybrid). The number of reports on CNT nanohybrids or nanocomposites is countless and the range of applicative fields is very wide. It turns out that CNTs have beneficial effects not only as physical supports, but also by electronic crosstalk with catalytically active species, thus resulting in higher performance.<sup>41</sup> A tentative classification can be made to group these materials into three most prominent categories, featuring CNTs/molecular metal catalysts, CNTs/metal nanoparticles (MN/CNTs) and CNTs/transition metal oxides (MO<sub>x</sub>/CNTs). Synthetic strategies rely on *in situ* or *ex situ* methods. The former indicate the assembly of inorganic compounds directly on the pristine (or modified) CNTs, while the latter refer to preformed metal nanoparticles, oxides or molecular complexes that are attached to nanocarbon supports by covalent or non-covalent bonding or electrostatic forces. A special class of composites or hybrids involves the combination of three or more building blocks to form materials that exhibit improved properties in a hierarchical order. We refer to these materials as hierarchical systems and we will provide a very restricted account of them at the end of this section.

### Molecular catalysts

**Functionalization of CNTs for anchoring molecular catalysts for catalysis.** The most typical strategy to attach a molecular entity to CNTs is to exploit *ad hoc* functional groups introduced during a CNT pre-functionalization step. Such groups can bind the metal complex by ligand exchange or electrostatic interaction. These systems are an interesting class as they retain many of the advantages of homogeneous molecular catalysts while bringing them into a heterogeneous phase, therefore allowing recyclability of the catalysts.

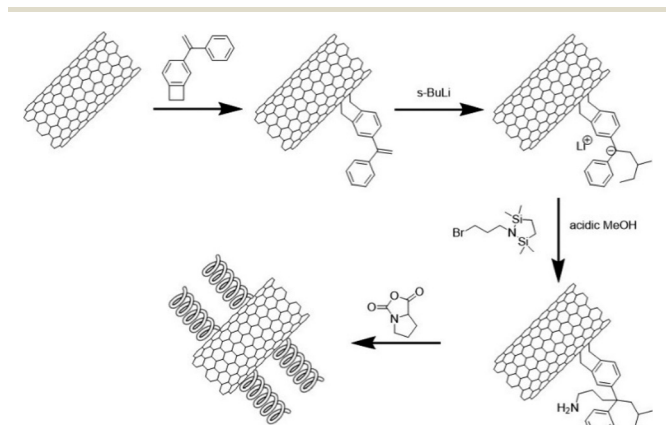


Fig. 3 Synthesis of the amino functionalized CNTs followed by surface initiated ring-opening polymerization of LP-NCA.<sup>38</sup>

Depending on the specific catalyst, the design of the anchor groups on the CNT sidewalls requires careful examination.

Carboxylic groups formed during CNT oxidation are versatile anchor points for several metal complexes. Wilkinson's catalyst featuring the  $\text{RhCl}(\text{PPh})_3$  complex was attached to o-SWCNTs by means of the carboxylic acid moieties and was successfully tested in the hydrogenation of cyclohexene at room temperature.<sup>42</sup> However, it has been pointed out that oxidative treatments often lead to degraded electronic properties of the CNTs, therefore an optimum balance has to be found depending on the particular catalytic process.

More sophisticated linking bridges of variable lengths have also been designed, relying on various types of coupling reactions. For example, cyanosilylation of aldehydes by a SWCNT/styryl functionalized vanadyl Schiff base catalyst was reported, with the catalyst prepared by a radical chain mechanism using a mercapto-modified SWCNT (Fig. 4).<sup>43</sup>

In a recent report, a rhodium complex was covalently attached to CNTs previously modified with a chiral pyrrolidine-based diphosphine ligand. The supported chiral complex effectively catalyses the enantioselective hydrogenation of methyl 2-acetamidoacrylate and  $\alpha$ -acetamidocinnamic acid.<sup>44</sup>

A number of other complexes were attached to the CNT scaffold, providing a platform for the establishment of a new class of supported homogeneous catalysts for a range of organic transformations. In principle, the type of CNT/molecular catalyst is only limited by creativity, although we have to be reminded that classical organic and organometallic chemistry of CNTs seems to suffer yet from limitations determined by the inherent structural characteristics of CNTs. Reactions proceed often uncontrolled or with more difficulty and it is not always possible to use that subtlety required by coordination chemistry for metal complex formation. However, with the progress of the "know-how" for the modification of CNTs, coupled with more in-depth theoretical knowledge, we foresee that more and more systems with specific catalytic functions will rapidly become available.

**H<sub>2</sub> production.** Another actively sought field of application is the energy sector, where enormous progress has been

achieved in the past few years. Over the last decade, H<sub>2</sub> production has become one of the most explored catalytic processes, given the great appeal of H<sub>2</sub> as a new environmentally friendly energy vector. By equipping a bioinspired Ni bis(diphosphine) complex with a pendant pyrene moiety, it was possible to non-covalently adsorb such metal species on the sidewalls of pristine MWCNTs through  $\pi$ -stacking. The adsorption proved to be robust enough to sustain electrocatalytic activation of water reduction to produce hydrogen, with performance comparable to that of platinum catalysts, but with the extra advantage of being tolerant towards CO.<sup>45</sup> It is worth noting that in a previous study, the authors had used a covalently modified MWCNT support to graft the active species, but this methodology turned out to be less convenient, given the limited amount of catalyst that could be loaded. In contrast, by exploiting the  $\pi$ -stacking strategy, a monolayer of the nickel complex could be formed, allowing fine-tuning of the electrode characteristics. This fact introduces a fundamental problem with regard to CNTs/molecular catalysts, namely the difficulty in many cases to reach adequate levels of metal complex binding. In the last example, the non-covalent approach guarantees a better coverage of the CNT scaffold. In other situations, this is not achievable, given the inherently weaker bond energy of the non-covalent linkages, and the metal complex loading remains too low to lead to detectable catalytic activities under normal conditions. Moreover, it often turns out that the actual CNT-molecular catalyst interaction is not precisely understood. Powerful characterization techniques such as solution NMR are not viable for these materials, leaving doubts about the exact nature of the bond. However, whenever possible, a set of other advanced characterization techniques can provide the essential structural information.

Other than  $\pi$ -stacking, another synthetic strategy to afford CNTs/molecular catalysts is to exploit electrostatic interactions. An ingenious catalyst able to perform the high-energy demanding process of water oxidation was obtained based on the attachment of a Ru polyoxometalate (Ru<sub>4</sub>POM) onto conductive MWCNTs. The assembly of the oxygen-evolving catalyst made use of the polyanionic nature of the Ru<sub>4</sub>POM, which could be electrostatically bound to positively charged MWCNTs. The latter, in turn, were accessed through decoration with protonated polyamidoamine (PAMAM) ammonium dendrimers.<sup>46</sup> The system is a milestone in the fascinating possibility of performing artificial water splitting using CNT-based catalysts. One step further would be to replace the applied electric current bias with a totally renewable source such as light, thus moving towards the tantalizing prospect of artificial photosynthesis. This is currently one of the hottest topics in energy-related research.

**Other energy and environmental processes.** The concept of non-covalent bonding of molecular catalysts through pyrene pendants was also exploited for water oxidation reaction by constructing a CNT/molecular catalyst featuring the complex  $\text{Ru}(\text{bpa})(\text{pic})_2$  (*i.e.* 2,2-bipyridine-6,6-dicarboxylic

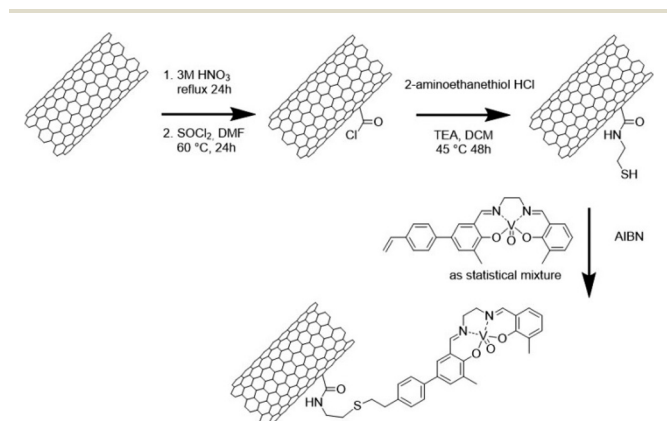


Fig. 4 Functionalization of oxidized CNTs with a vanadyl catalyst.<sup>43</sup>

acid, H<sub>2</sub>bpa; 4-picoline, pic) able to perform water oxidation with reported TOFs exceeding 1700 cycles per h (Fig. 5).<sup>47</sup>

Pyrene moieties have been often exploited as non-covalent anchor groups with other transition metals for several energy processes. For instance, an electrode featuring CNTs supporting an iridium dihydride complex immobilised through a pyrene group was prepared and exhibited good performance and high selectivity in the electroreduction of CO<sub>2</sub> to formate (Fig. 6).<sup>48</sup> CO<sub>2</sub> reduction has indeed become another crucial reaction from an environmental point of view, in line with the ever more stringent regulations on CO<sub>2</sub> emission in the atmosphere.

**General considerations and future prospects.** In the vast majority of cases, it seems that CNTs exclusively have the role of physical supports. The same considerations made for metal-free CNT catalysts with regard to both purity and cost of CNTs apply here. The presence of metal impurities can be critical in view of the expected enantio-, stereo- or chemo-selectivity of some processes. Besides, potential leaching of these metals can be detrimental in terms of quality of the products, especially in the case of fine chemicals or pharmaceutical compounds. In addition, given the cost of CNTs in comparison with that of standard supports such as AC, we foresee that large-scale production of such catalysts is still an obstacle. However, the preparation of fine chemicals is one sector where they could find widespread application in the near future. Furthermore, the exact relationship between the active metal species and the extended  $\pi$ -systems still lacks a full understanding through mechanistic studies. It is envisioned that major advantages could be obtained if such relationship is more comprehensively understood.

### Supported metal nanoparticles

There is a plethora of systems based on the deposition of metal nanoparticles on CNTs and a comprehensive review is beyond the scope of the present work. In this sub-section, we will limit our report to the identification of general research trends and pinpoint some representative examples.

**Hydrogenation.** Hydrogenation of organic substrates is amongst the most investigated reactions featuring catalysts

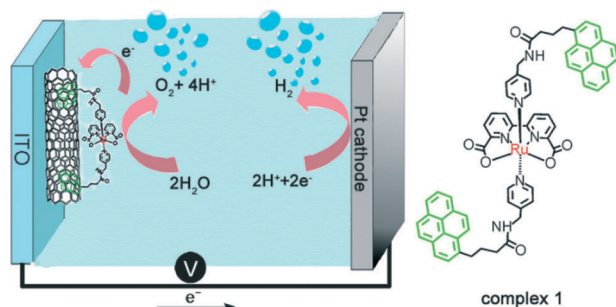


Fig. 5 Non-covalent interactions mediating the binding of Ru(bpa)(pic)<sub>2</sub> (i.e., complex 1) to CNTs for efficient electrocatalysis of water splitting. Reprinted with permission from ref. 47. Copyright © 2011 Wiley-VCH.

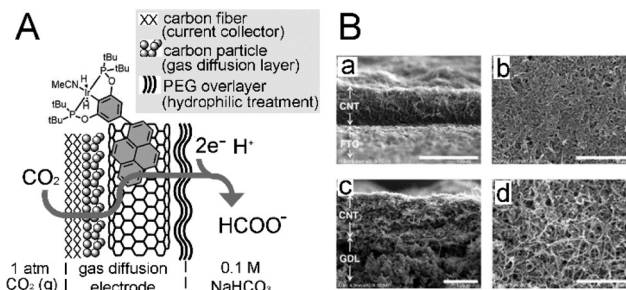


Fig. 6 (A) Scheme of the molecular catalyst/carbon nanotube-coated gas diffusion electrode for electrochemical reduction of CO<sub>2</sub> to formate. (B) SEM images of the catalyst thin films on FTO (a, b) and GDL (c, d). Left (a, c): cross-section; right (b, d): top view. Adapted with permission from ref. 48. Copyright © 2014 Wiley-VCH.

based on Ru, Pd, Pt, Au, and Rh deposited on CNTs. Cinnamaldehyde has served as a model molecule for hydrogenation to evaluate the activity and selectivity of the catalysts. Ru/CNTs are effective in reducing cinnamaldehyde to cinnamyl alcohol<sup>49,50</sup> or hydrocinnamaldehyde<sup>51</sup> depending on the catalyst preparation method, confirming the delicate structure/activity relationship. The same consideration on the activity and selectivity applies to systems featuring Pd (ref. 52) and Pt (ref. 53) as metal active species. Similarly, reduction of nitrobenzene is a good probe reaction to evaluate the hydrogenation potential of the catalysts. This reduction has been attained with various metal nanoparticles deposited on CNTs using a series of methods.<sup>54–56</sup> Many other substrates have been successfully reduced by CNT/noble metal nanocomposites and it appears that in many cases, the good dispersion of the MNs onto the CNT backbone is responsible for the higher activities. Control over the size and distribution is crucial and can be reached to a good extent depending on the preparative protocol. Indeed, a proper correlation between activity and structural parameters cannot be obtained without a very uniform particle size distribution (close to monodispersity). Further studies are needed to fully understand the metal-support interaction in these f-CNTs in order to improve metal nanoparticle adhesion, promote electronic interaction, as well as prevent metal leaching during reaction.

**Oxidation.** Oxidation represents another class of well-established reactions catalysed by MN/CNTs. In this case, alcohols are used as model molecules to test the activity and selectivity. For instance, oxidation of benzyl alcohol to benzaldehyde was examined using 2 nm Ru nanoparticles deposited on CNTs by an impregnation/reduction method. These hybrids turned out to be considerably more active than the corresponding Ru nanoparticles deposited on TiO<sub>2</sub> or AC, with a TOF of 178 h<sup>-1</sup>.<sup>57</sup> Similarly, Au NPs deposited on o-CNTs turned out to be more active than Au NPs deposited on other supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, graphite, MgO, etc. in the oxidation of cellobiose to gluconic acid.<sup>58</sup>

As for the CNTs/molecular catalysts, the function of the CNTs is primarily that of a support, providing good

dispersion and stabilizing the NPs towards aggregation/sintering. However, many studies have indicated that there may be electronic communication between the NPs and the carbonaceous framework. Shanahan *et al.* fabricated Au NPs supported on SWCNTs and used them in the oxidation of secondary alcohols with a 95% efficiency; by means of UV-vis absorption experiments, they related the high activity to electron transfer from the Au NPs to the SWCNTs.<sup>59</sup> Given the vast efforts devoted to the assembly of MN/CNTs, we believe that now is the time to dedicate future studies to a higher level of fine-tuning of deposited metal nanoparticles. For example, engineering specific crystal facet exposure could improve selectivity towards oxidation or hydrogenation through control of the adsorption mode of the specific reactive substrate. Of particular interest is the possibility to conduct asymmetric hydrogenation. Thus far, this possibility has been demonstrated in the presence of an appropriate chiral modifier such as cinchonidine. For instance, Pt NPs deposited on SWCNTs modified with cinchonidine were found to be active in the asymmetric hydrogenation of ethyl pyruvate to (*R*)-ethyl lactate with moderate enantioselectivity.<sup>60</sup>

**C–C coupling reactions.** Thus far, the class of reactions involving C–C bond formation by Pd/CNT catalysts has been particularly studied. Indeed, typical Suzuki, Sonogashira and Heck couplings have been conducted with a decent degree of success. The Suzuki coupling of phenylboronic acid and 1-iodo-4-nitrobenzene to nitro biphenyl was attained with 94% conversion after 30 min and a TOF of 709 h<sup>-1</sup>.<sup>61</sup> The report is particularly interesting because of the simple method of preparation of the catalyst based on supercritical CO<sub>2</sub> which was reported earlier by the same authors.<sup>62</sup> The aspects of the preparative method need to be thoroughly considered, as they can lead to dissimilar activities derived from different particle sizes, different metal dispersions and other features. This was demonstrated by Corma *et al.* who evaluated the Suzuki coupling of phenylboronic acid and iodobenzene with three catalysts prepared using three synthetic protocols. Despite the variation in activities of the three materials, it turned out that they all exhibited higher activity than Pd deposited on activated carbon.<sup>63</sup> For these reactions, great attention must be paid to excluding the contribution of the homogeneous reaction by slow metal leaching.

Better performance for the Heck coupling reaction between 4-iodoanisole and styrene by Pd/CNT catalysts as compared to Pd/C was also found.<sup>64</sup> Similarly, several Sonogashira coupling reactions were reported, including those employing Pd/CNT catalysts working under “eco-friendly” copper-free conditions, which could be efficiently recycled.<sup>65,66</sup>

**Electrocatalytic reactions.** As for the metal-free CNT catalysts, one very important field of application is electrocatalysis. In particular, the assembly of MN/CNT-based electrodes for fuel cells has been very much explored. In many cases, the presence of CNTs leads to improved performance of the electrode, which is a consequence of the excellent conduction properties of the graphenic framework,

because they allow better tailoring of the electrode surface. ORR is a classical process studied with these systems and many examples are available. Most systems are based on Pt, on the account of the high activity of Pt towards ORR. For instance, higher rate constants for ORR were achieved with a Pt/SWCNT-based electrode compared to the corresponding Pt/C electrode. The key to this finding was the high porosity of the SWCNTs, which allowed more facile diffusion of the reactants, and the increased electrode stability caused by the SWCNTs.<sup>67</sup>

More recently, Pt NPs were electrodeposited using the microcapillary electrochemical method (MCEM) on a SWCNT electrode, whose presence allowed precise control over the electrode surface coverage and the specific surface area of the Pt NPs. Upon tailoring these two parameters, a comparable activity to that of bulk Pt for ORR was achieved (Fig. 7).<sup>68</sup>

An environmentally friendly approach to attach Pt NPs onto CNTs makes use of ionic liquid polymer thin films, which produce the beneficial effect of layering around the Pt NPs. This approach avoids agglomeration and results in

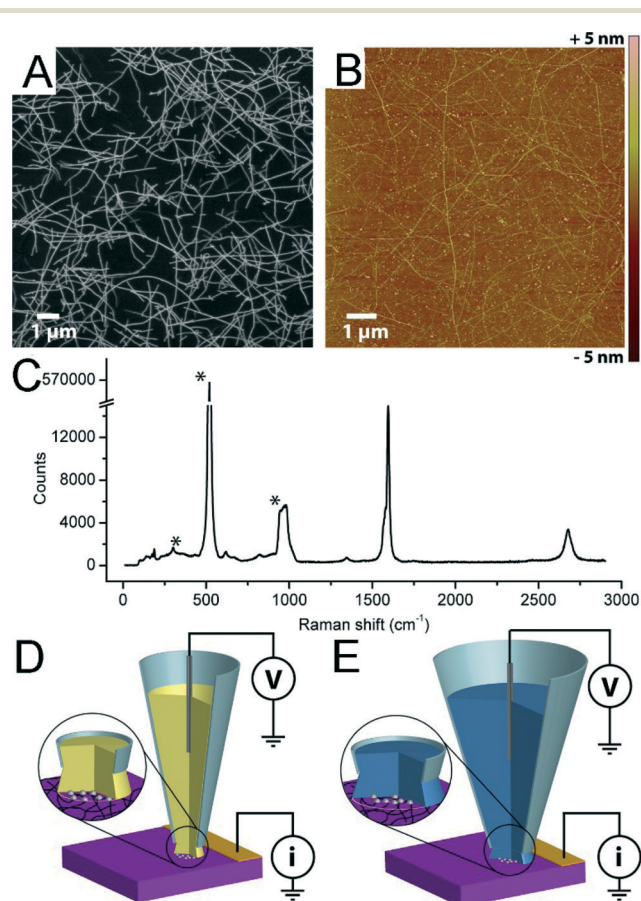


Fig. 7 E-SEM (A) and AFM (B) images of electrodeposited Pt NPs on SWCNTs and (C) the corresponding micro-Raman spectrum. Peaks marked with \* are related to the Si/SiO<sub>2</sub> substrate. (D) Schematic of Pt NP electrodeposition using MCEM. (E) Schematic of the setup used to measure ORR and MOR. Reprinted from ref. 68. Copyright © 2014, with permission from Elsevier.



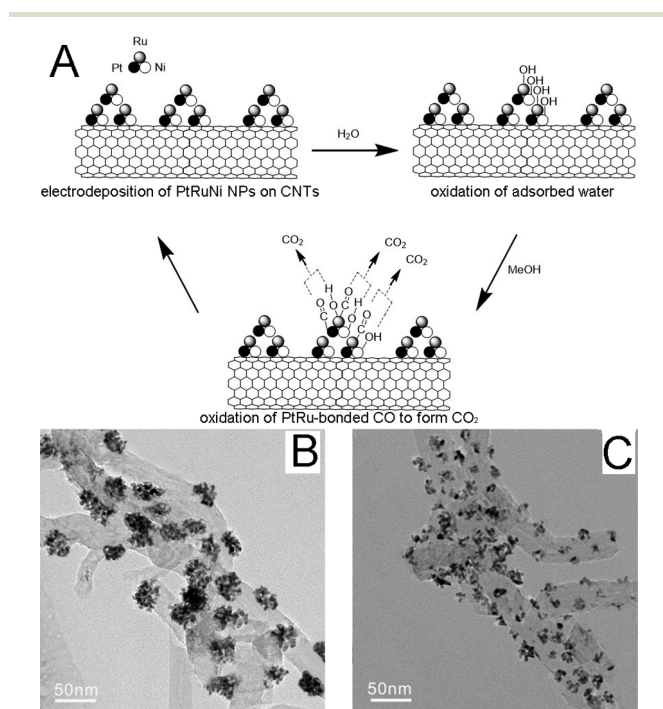
longer-term operational stabilities for methanol oxidation by the assembled electrode.<sup>69</sup>

Despite the large number of Pt/CNT systems, a new trend can be identified where the metal nanoparticles are based on more available and less costly metals, or at least attempts to reduce the Pt content by alloying with cheaper metals. Iron seems to be the most likely candidate for future developments, and electrodes with Fe/CNTs are slowly making their breakthrough. A very notable example is the preparation of CNT/Fe<sub>3</sub>C NP hybrids by annealing a mixture of melamine, PEG-PPG-PEG Pluronic P123, and Fe(NO<sub>3</sub>)<sub>3</sub>. The resulting material exhibited a half-wave potential of 0.861 V for ORR, almost 50 mV more positive than that of a 20 wt% Pt/C catalyst.<sup>70</sup> However, most efforts are devoted to the use of iron oxides, given the more facile oxidation of Fe nanoparticles as compared with Pt. Alternatively, the possibility of internalising the Fe NPs inside the CNT channels appears to be more promising (see the next section). Alloying Pt with other metals is another interesting opportunity, as the resulting nanoparticles combine the diverse properties of the different metals, while decreasing the content of expensive Pt. Deposition of Pt–Ru and Pt–Ru–Ni nanoclusters on MWCNTs was achieved electrochemically and the resulting electrodes were tested for ORR and methanol oxidation reaction (Fig. 8). The ternary metal catalysts exhibited higher activities, and the authors attributed them to the bifunctional mechanism in place and the 3D microflower structure of the nanoclusters. Moreover, the presence of MWCNTs contributes to the

activity through the electrochemically generated oxygen functional groups.<sup>71</sup>

**Other reactions.** A co-impregnation method has also been used to support other bimetallic nanoparticles on CNTs, such as the catalyst RuFe/CNT, which was active in the hydrogenolysis of glycerol to 1,2-propanediol and ethylene glycol. A comparison with the corresponding monometallic Ru/CNTs demonstrated a more pronounced efficiency of the bimetallic system towards C–O breakage, resulting in higher selectivity towards glycol products, whereas the monometallic system favours C–C cleavage, thus leading to large amounts of CH<sub>4</sub>.<sup>72</sup>

**General considerations and future prospects.** In general terms, as compared to molecular catalysts, MNs deposited on CNTs have enjoyed so far even higher popularity, mostly on the account of the wider range of preparative protocols, which in many cases are very simple, but also because of the more direct characterization methods available above all microscopy techniques. As illustrated above, the range of catalysed reactions is broad. Hydrogenation and oxidation reactions keep proliferating and the scope of reactions has become wider and wider. Other than simple molecules of industrial interest (for instance in the polymer industry), a notable goal would be their future breakthrough in highly selective hydrogenation or oxidation steps in the production of fine chemicals, for example in the multi-step synthesis of complex biomolecules. On the other hand, the electrocatalysis field is approaching a level that goes beyond fundamental studies, and the design of electrodes from an engineering point of view, namely for real fuel cell construction, seems to be well within reach.



**Fig. 8** (A) Scheme for the mechanism for Pt–Ru–Ni/MWCNT electrode surface in methanol solution. (B, C) TEM images of (B) Pt–Ru (8 : 2) / MWCNT and (C) Pt–Ru–Ni (8 : 1 : 1) / MWCNT catalysts. Adapted from ref. 71 with permission from Elsevier. Copyright © 2014.

## Metal oxides

**TiO<sub>2</sub>/CNT catalytic systems.** A large variety of CNTs/metal oxides have been synthesised for catalytic purposes using a range of procedures. One of the most investigated systems has been TiO<sub>2</sub>/CNTs. The well-known photocatalytic properties of the semiconductor TiO<sub>2</sub> have inspired many groups to develop TiO<sub>2</sub>/CNT photocatalysts, which in many cases contribute to the improved photocatalytic performance. It is commonly accepted that the benefits of interfacing TiO<sub>2</sub> with CNTs are beyond simple improved structural stability. In one proposed mechanism, the CNTs act as efficient scavengers of photoexcited electrons from TiO<sub>2</sub>, retarding the electron/hole recombination rates by means of heterojunctions formed at the interface with the semiconductor. Alternatively, a role of the photosensitizer has been proposed, with the electron excited and injected from the CNTs into the TiO<sub>2</sub> conduction band and subsequent electron transfer from the TiO<sub>2</sub> valence band to the CNTs, forming a charge separation state (electron/hole) on TiO<sub>2</sub> (Fig. 9).<sup>73</sup>

Although the first mechanism is the most frequently mentioned today, some reports on the photocatalytic activity under visible light (despite TiO<sub>2</sub> being a UV active semiconductor) serve as a warning that careful examination of several

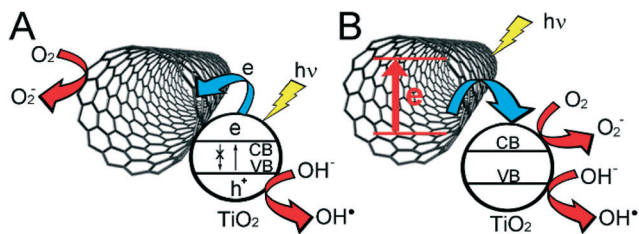


Fig. 9 The two possible functions of CNTs when hybridised with a semiconductor such as  $\text{TiO}_2$ . (A) Electron sink and (B) photosensitizer.<sup>73</sup>

aspects such as the specific reaction, the materials used and the preparative method, needs to be done before drawing rushed conclusions. The visible light-catalysed degradation of phenol by  $\text{TiO}_2/\text{MWCNTs}$  prepared *via* a modified sol-gel method is a remarkable example of the complexity of the mechanism, where the authors made use of the photosensitizing effect of the CNTs.<sup>74</sup> However, in a report about the visible light catalytic photoelectroactivity of a  $\text{TiO}_2/\text{CNT}$ -modified ITO electrode for the degradation of phenol, XPS investigations indicated the presence of Ti–C and Ti–O–C bonds formed during calcination by substitution of the oxygen and titanium atoms with C. The visible light efficiency was thus attributed to this “doping” effect, rather than to the photosensitizing role of the CNTs.<sup>75</sup> In conclusion, considering the large number of  $\text{TiO}_2/\text{CNT}$  catalysts, it is apparent how much further studies, perhaps involving more sophisticated techniques such as transient absorption spectroscopy or other *in situ* spectroscopic techniques, combined with chemical test reactions, are needed. All these considerations can be extended in more general terms to all semiconductor  $\text{MO}_x/\text{CNT}$  systems.

Regardless of the exact role, however, it is clear from experimental evidence that the direct participation of the CNTs in the photocatalytic process exists. For this reason, it is imperative that contact between the two phases is maximised in terms of both vicinity and CNT area covered. Synthetic strategies have already reached a good level of control, but more reliable and reproducible protocols are always in demand. Other advantages derived from the presence of CNTs are related to the maximisation of the semiconductor area exposed to light, and therefore optimised light absorption and increased quantum efficiency.

Most reports on  $\text{TiO}_2/\text{CNTs}$  have focused on the degradation of pollutants. Other than phenol, substrates such as methylene blue (MB),<sup>76</sup> methyl orange,<sup>77</sup> indigo carmine,<sup>78</sup> and many other molecules have been tested. Probably, the literature has almost reached saturation and therefore unless some exceptional performance is noted, some peculiar effects are observed or visible light activity is found, we feel that interest should shift towards other photoactivated processes, in particular those related to energy.  $\text{H}_2$  evolution is a potential field, so far being successfully exploited by using mainly hierarchical systems (see the next section), where  $\text{TiO}_2/\text{CNTs}$  are further modified with metal nanoparticles to enhance

their activities.  $\text{CO}_2$  photo-reduction is another important energy and environmental application. Reduction of  $\text{CO}_2$  by  $\text{TiO}_2/\text{MWCNTs}$  under UV irradiation has so far been reported for composites prepared through sol-gel or hydrothermal methods, where an electron dispersing role (retarding charge recombination) was assigned to the MWCNTs. The authors also explained how the diverse phases of  $\text{TiO}_2$ , formed according to the synthetic method used, are correlated with the selectivity towards a specific product.<sup>79</sup> More recently, a catalyst working under visible light was synthesised through a simple coating approach, and promising, although not excellent, activities for the photo-reduction of  $\text{CO}_2$  to methane were observed.<sup>80</sup>

**Other  $\text{MO}_x/\text{CNT}$  catalytic systems.** As a common alternative to  $\text{TiO}_2$ , another frequently employed photoactive metal oxide that has been combined with CNTs is ZnO. As for  $\text{TiO}_2$ , research on photocatalysis has mostly been devoted to the abatement of water contaminants, such as methylene blue<sup>81</sup> or Rhodamine B.<sup>82</sup> Other metal oxides have been reported as photocatalysts.

In analogy with CNTs/molecular metal catalysts and MN/CNTs, construction of electrodes with  $\text{MO}_x/\text{CNTs}$  for electrocatalytic applications has been fast developing. A poly(sodium 4-styrene sulfonate)-assisted route gave access to  $\text{MnO}_2/\text{MWCNTs}$  that exhibited moderate activity towards the four-electron reduction of oxygen in alkaline media with no further precious metal required.<sup>83</sup> The same process was also achieved by catalysts prepared by growing  $\text{Co}_3\text{O}_4$  nanocrystals on N-doped CNTs.<sup>84</sup> More recently, a series of  $\text{MO}_x$  ( $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , NiO, CuO, and  $\text{Fe}_x\text{O}_y$ ) loaded onto N-doped CNTs *via* an impregnation method exhibited activities comparable to those of carbon-supported Pt-based catalysts for ORR in alkaline media, as well as the oxygen evolution reaction, and dependent on the specific morphology of the catalysts.<sup>85</sup> These examples demonstrate that with an appropriate choice of  $\text{MO}_x$  and synthetic conditions, precious metal-free  $\text{MO}_x/\text{CNT}$  electrodes can be assembled and successfully used for specific purposes. On the other hand, the assembly of electrochemical sensors or supercapacitors based on  $\text{MO}_x/\text{CNTs}$  represents a fruitful field of research worthy of further exploitation. Among others, examples with  $\text{Fe}_3\text{O}_4$ ,<sup>86</sup>  $\text{RuO}_2$ ,<sup>87,88</sup>  $\text{WO}_3$ ,<sup>89</sup> and in particular  $\text{SnO}_2$ ,<sup>90–93</sup> have been reported.

Although photo- and electro-catalysis are predominantly explored, standard heterogeneous catalysis falls within the scope of reactions catalysed by  $\text{MO}_x/\text{CNT}$  systems, and it is a field that merits deeper investigation. This is substantiated by several examples in the literature, such as methanol oxidation by a  $\text{RuO}_2/\text{MWCNT}$  catalyst prepared through an oxidation-precipitation method,<sup>94</sup> and the highly active and selective dehydrogenation of ethylbenzene by  $\text{Fe}_2\text{O}_3/\text{CNTs}$ .<sup>95</sup>

In contrast to MN/CNTs, which offer many examples in several catalytic processes, recent trends seem to address  $\text{MO}_x/\text{CNTs}$  as platforms for the assembly of more complex systems with improved performance (hierarchical systems). Apart from  $\text{TiO}_2/\text{CNTs}$ , there are not as many examples of the direct use of  $\text{MO}_x/\text{CNTs}$  in catalysis available as compared to

MN/CNTs, although the bulk of reports is not negligible, particularly for photocatalytic applications. Synthesis of  $\text{MO}_x/\text{CNTs}$  generally implies the use of higher metal oxide loadings as compared to that of metal nanoparticles, therefore the resulting hybrids or composites show structures where the oxide more or less uniformly envelops the CNTs. It is worth noting that the standard preparative methods in many cases yield materials with poor homogeneity, with the presence of considerable amounts of the free standing metal oxide, which can severely affect reproducibility of the catalytic activity. This aspect requires careful addressing through development of new synthetic methodologies, optimization of the existing methods or adequate purification strategies to avoid non-homogeneous nanocomposites (Fig. 10).

### Hierarchical systems

While the trends and perspectives for the binary MN/CNT and  $\text{MO}_x/\text{CNT}$  systems have been clearly identified, the possibility to create hybrids by combination of three (or more) building blocks elevates the catalytic scope to a completely different level. The concept of hierarchical systems stems from the precise role that each building block has in the catalytic process under investigation. As the structural complexity of the catalyst augments, so does the difficulty in its preparation. However, the obstacles arising from the assembly step are often compensated by a considerable enhancement of the catalytic functionality. Most frequently, the catalysts consist of ternary systems  $\text{NM}/\text{MO}_x/\text{CNTs}$ .

In this short section, we do not intend to treat the hierarchical catalysts in a systematic way, as we feel that some dedicated reviews should fulfill the hard task of a comprehensive study. We will just mention a few representative examples including some of the activities of our research group into this field.

As a common example, we can take the assembly of Pt/ $\text{TiO}_2/\text{CNT}$  materials used in photocatalytic hydrogen evolution. The addition of Pt nanoparticles to the  $\text{TiO}_2/\text{CNT}$  composites results in a very significant increase of the catalytic activity. The often applied mechanism is based on the

injection of the photoexcited electrons of  $\text{TiO}_2$  into the Pt orbitals, where the catalytic reduction reaction actually occurs. The consequences of this electron transfer are the reduced recombination rates of the separate charges and in turn the enhancement of activity. This has been shown in a few reports on hydrogen evolution from water solution in the presence of a sacrificial electron donor.<sup>96–98</sup> Other less precious metals such as Ni or Pd can also be proficiently used for this purpose.<sup>99</sup> Solvent-free oxidation of benzyl alcohol was achieved with good selectivity using a hierarchical CNT/ $\text{MnO}_x/\text{Pd}$  catalyst (Fig. 11), where  $\text{MnO}_2$  was first immobilised *via* impregnation on the CNT support, followed by deposition of Pd nanoparticles. The ternary catalyst showed improved performance attributed to more facile electron transfer at the  $\text{MnO}_x$ -Pd interface and promotion of oxygen activation through lattice oxygen transport onto the active sites. The stability was excellent, due to the hybridization of the metal oxide with the CNT scaffold.<sup>101</sup>

**Core-shell systems.** In our efforts devoted to the synthesis of hierarchical hybrid systems incorporated with CNTs, we have developed a sol-gel strategy where it is possible to envelop CNTs in layers of a metal oxide phase ( $\text{CeO}_2$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) embedding noble metal nanoparticles (Pd, Pt). The synthesis features the pre-assembly of the binary inorganic phase into a core-shell structure ( $\text{MN}@\text{MO}_x$ ) where the noble metal is surrounded by a metal alkoxide precursor, which is then reacted with appropriately functionalised MWCNTs. Final controlled hydrolysis produces a hierarchical  $\text{NM}@\text{MO}_x/\text{MWCNT}$  hybrid (Fig. 12). We have proven that the structure of the hybrid, with the core-shell hierarchy of the inorganic matrix, contributes to the improved stability of the system, which is also reflected in its higher activity. The catalyst bears remarkable versatility, and depending on the metal and metal oxide used, it can be proficiently employed for a defined purpose. We successfully performed photo-reforming of methanol, water-gas shift reaction and Sonogashira coupling.<sup>102</sup>

We also recently demonstrated how the system may be further improved for a specific process by means of thermal

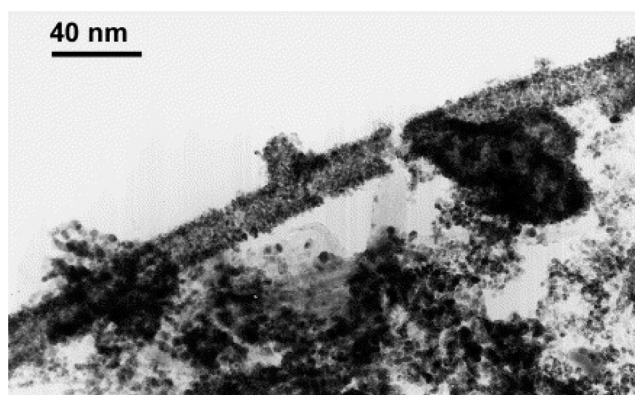


Fig. 10 TEM image of a non-homogeneous nanocomposite. Reprinted from ref. 100 with permission from Elsevier. Copyright © 2002.

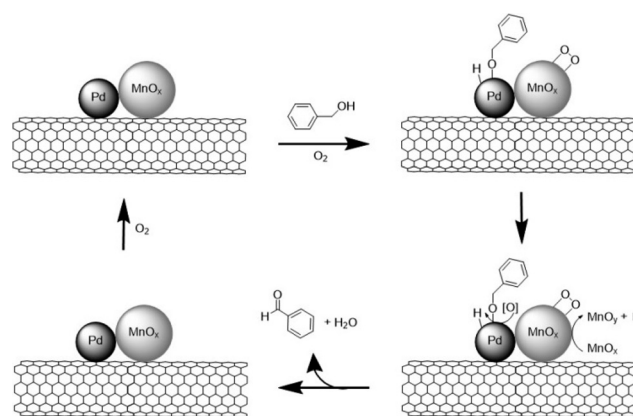
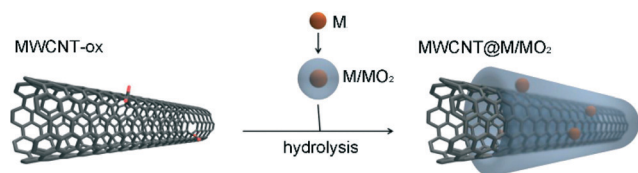


Fig. 11 Solvent-free oxidation of benzyl alcohol achieved with good selectivity using a hierarchical CNT/ $\text{MnO}_x/\text{Pd}$  catalyst.<sup>101</sup>



**Fig. 12** Synthesis of core-shell systems featuring the pre-assembly of the binary inorganic phase into a core-shell structure where the noble metal (M) is surrounded by a metal alkoxide precursor, which is then reacted with appropriately functionalised MWCNTs. Final controlled hydrolysis produces a hierarchical MWCNT@M/MO<sub>2</sub> hybrid. Reprinted with permission from ref. 102. Copyright © 2012 American Chemical Society.

treatment, and how the homogeneity of the catalyst, which depends on the relative composition, becomes an essential parameter to consider during the catalyst formulation phase.<sup>103</sup>

The NM@MO<sub>x</sub> phase can also feature the same transition metal. In a latest example, a remarkable activity for electrocatalytic hydrogen evolution, comparable to that of platinum, was reported for a catalyst consisting Ni@NiO/CNTs. The authors ingeniously exploited the CNT catalyst to cause the decomposition of the external Ni nanoparticles to generate a thin shell made of NiO nanoparticles. The existence of the inorganic heterostructure, as well as the interfacing between NiO and CNTs which impedes complete reduction, is key to the outstanding activity.<sup>104</sup>

**Considerations on hierarchical systems.** From the above examples, it is obvious that switching to ternary (or higher) systems increases the degree of complexity not only of the synthetic phase, but also of the resulting mechanism of action. The range of possibilities arising from the utilization of hierarchical catalysts is much wider, provided that the assembled architecture is carefully designed in order to exhibit defined functionality.

## Confined space

### Role of CNTs in catalysis

An intriguing possibility arising from CNTs that cannot be offered by most of other carbon nanostructures is the endohedral filling with catalytically active species which has been known for more than a decade.<sup>105</sup> Indeed, the inner cavity of CNTs can be subjected to modification with other entities to produce what is sometimes referred to as the *confinement effect*.<sup>106</sup> The definition aims at explaining the different behaviours of compounds deposited outside or inside the CNTs. As a representative example, two hybrids with Pt nanoparticles deposited inside or outside the MWCNT channel were prepared and tested for the asymmetric hydrogenation of ethyl pyruvate in the presence of cinchonidine as a chiral modifier. It turned out that the former catalyst could reach a TOF as high as 100 000 h<sup>-1</sup> and 96% ee, as opposed to 15 000 h<sup>-1</sup> and 75% ee of the latter.<sup>107</sup>

Several aspects have been examined, such as the higher  $\pi$ -electron density on the outer layer of the MWCNTs due to

the graphene curvature, as shown by TPR, CO adsorption microcalorimetry, and first principles calculations of Ru nanoparticles deposited on the interior or the exterior of CNTs.<sup>108</sup> An enhanced pressure of the reactants in the nano-sized channels has also been proposed.<sup>109</sup> Two more explanations could be related to a diminished agglomeration tendency of the metal catalysts in the confined space as compared to that of the outer particles<sup>110</sup> and an increase of turnover numbers as a consequence of a higher frequency of adsorption of the reactant molecules. However, this latter hypothesis is weakened by considering the restriction posed by the nanotube walls to the free in/out transfer of reactants and products.

Despite the many studies as well as controversies, the reactivity trends are still difficult to predict, and they seem to be dependent on a large number of factors, above all the type of catalyst and the specific process under investigation. For example, if confinement of Rh, Mn, Fe, and Li appears to be beneficial for ethanol generation from syngas (Fig. 13),<sup>111</sup> outer Ru nanoparticles are more efficient in ammonia decomposition than the internalised ones.<sup>112</sup>

In any case, findings on CNT catalyst confinement seem to point towards a still relatively unexplored and worthwhile field of research, with a wide range of catalytic applications. Standard Pd-catalysed C–C cross-coupling such as the Suzuki coupling reaction has been reported in water, with the embedded Pd nanoparticles showing much higher resistance towards sintering.<sup>113</sup> This might spark interest to those groups interested in industrially relevant processes. The decomposition of ammonia to produce H<sub>2</sub> proved to be a useful test reaction, particularly benefiting from the structural features of the nanohybrids, and other than with Ru, it has been proven to be achievable also with more cost-effective CNT-encapsulated bimetallic particles, such as Fe–Co alloys (Fig. 14).<sup>114</sup>

As a special case of metal nanoparticles deposited on CNTs, endohedral MN/CNTs are also being investigated in hydrogenation reactions that, as we explained earlier, represent an established class of reactions for standard exohedral MN/CNTs. In the case of CNT-confined MNs, however, asymmetric hydrogenation could be a more favourable prospect because of the unique properties of the nanochannels. Very recently, 96% ee and a TOF as high as 105 h<sup>-1</sup> were reported for the asymmetric hydrogenation of  $\alpha$ -ketoesters by a catalyst comprising endohedral Pt nanoparticles/CNTs in the presence of cinchonidine as a chiral modifier.<sup>107</sup>

The function of the CNTs not only could be that of nano-reactors, but could also be related to the active participation in the specific catalytic reaction. An interesting prospect is to exploit the electronic communication between the endohedral metal and the conductive graphene multilayer structure for electrocatalytic reactions. By across-layer electron transfer from the Fe metal to the outer CNT layer, it is possible to carry out electrocatalytic ORR in acidic media at the external CNT surface. In this case, other than acting as an electron shuttle, the CNT scaffold provides protection for Fe

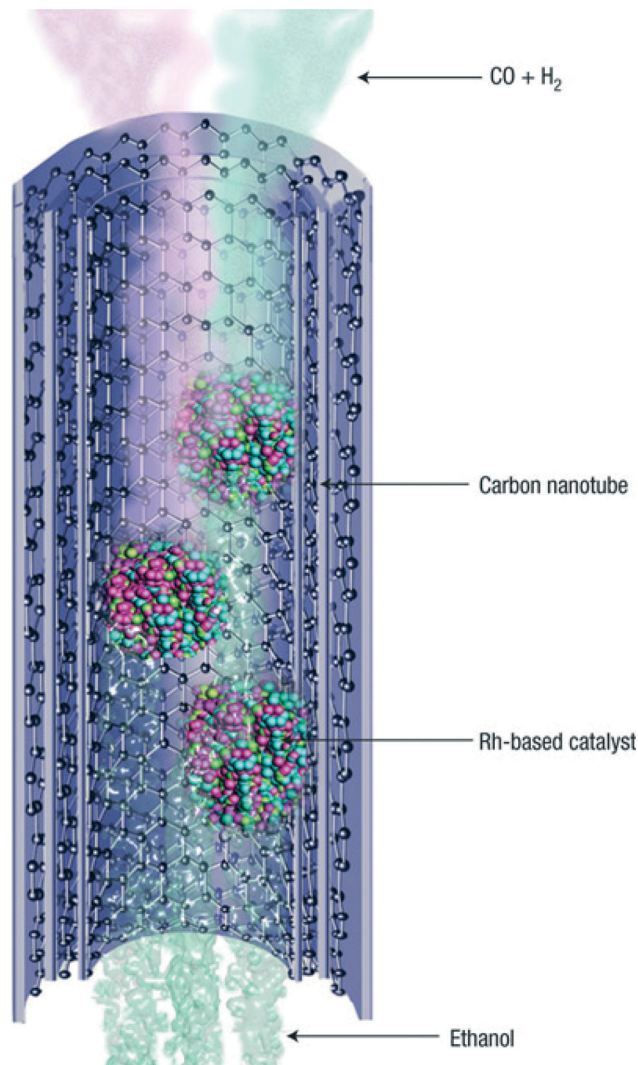


Fig. 13 Schematic diagram showing ethanol production from syngas inside Rh-loaded carbon nanotubes. Reprinted with permission from Macmillan Publishers Ltd. (ref. 111). Copyright © 2007.

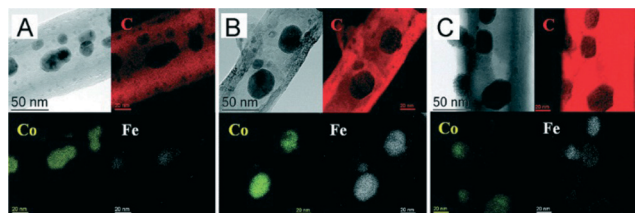


Fig. 14 Electron Energy Loss Spectroscopy (EELS) elemental mappings of fresh samples: (A) 5%  $\text{Co}_2\text{Fe}/\text{CNTs}$ , (B) 5%  $\text{CoFe}/\text{CNTs}$ , and (C) 5%  $\text{CoFe}_5/\text{CNTs}$ . Adapted with permission from ref. 114. Copyright © 2008 American Chemical Society.

towards leaching. This finding is of relevance to the development of new electrodes for polymer electrolyte membrane fuel cells (PEMFCs).<sup>115</sup> We extended this work, and recently discovered that functionalization of the outer shell of  $\text{Fe@MWCNTs}$  with benzoic acid groups through addition of radicals from diazonium salt intermediates results in a

catalyst capable of activating both ORR and HER under physiological conditions.<sup>116</sup>

### General considerations and future prospects

In our view, one aspect still requiring further improvements is the preparation of these peapod-like materials. Internalization of metals inside CNT channels using, for example, the classical microcapillary method<sup>117,118</sup> is not trivial and often leads to non-uniform materials, with the metal outside the CNTs needed to be removed. Alternatively, it appears that *in situ* methods, namely encapsulation of the metal during the production phase of the CNTs, are promising strategies which have greatly progressed, but still require better control.<sup>119</sup> Internalization of the molecular catalyst is also a fascinating and unexplored field.

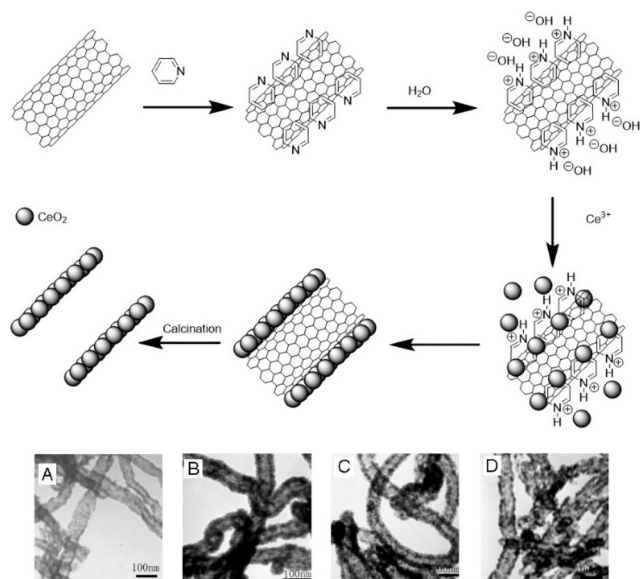
### Removable templates

An extra opportunity arises from the use of CNTs as templating agents for inorganic catalysts, in order to obtain 1D morphologies that can have a defined impact on catalysis. As the CNTs oxidise below the melting point of most metals, the all-carbon templates can be conveniently removed by combustion at about 500–600 °C (combustion temperature range of CNTs) if not specifically required for this purpose. In a classic example, surface tension effects drove the growth of crystalline  $\text{V}_2\text{O}_5$  layers along the outer CNT shell. Moreover, the metal oxide could grow inside the nanotubes as well as intercalate in between shells. The removal of the carbon scaffold by oxidation led to the preparation of layered  $\text{V}_2\text{O}_5$  fibres with desired widths.<sup>120</sup>

A variety of metal oxides have been investigated to prepare inorganic materials with CNT-induced tubular morphology. Key advantages of this synthetic approach reside in the single-crystalline materials obtained, and in their large dimensions, with lengths often extending well beyond those of the carbon template. Most likely, once 1D growth is initiated, the oxide is capable of continuing the growth along the preferential longitudinal direction.<sup>121</sup>

CNT removal by aerobic thermal treatment is generally not complete, as some of the carbonaceous material remains entrapped within the inorganic phase. This fact is not always detrimental, as the carbon debris can play a significant role in the catalysis, as has been demonstrated in CO oxidation by hollow  $\text{CeO}_2$  nanotubes prepared using CNTs as removable templates. Other than the impact induced by the 1D architecture, it turned out that the improvement in activity performance was also attributed to the remains of the CNTs after thermal treatment, as they act as dopants forming  $\text{CeO}_{2-x}\text{C}_x$  species, bearing  $\text{Ce}^{3+}$  ions (Fig. 15).<sup>122</sup>

However, in most cases, removal of the CNTs appears to be detrimental. We evaluated the water-gas shift reaction using different compositions of  $\text{Pd@CeO}_2/\text{MWCNTs}$  and made a comparison with the corresponding catalysts after CNT removal by calcination at 450 °C. Upon burning of the MWCNTs, the 1D morphology was retained. As calcination at



**Fig. 15** Proposed mechanism for the formation of CeO<sub>2</sub> nanotubes (reaction scheme on top). TEM images of CeO<sub>2</sub> nanotubes calcined for 30 min at (A) 450 °C, (B) 500 °C, (C) 550 °C, and (D) 600 °C for 10 h (bottom images). Adapted from ref. 122 with permission from Elsevier. Copyright © 2008.

higher temperatures resulted in higher crystallinity of the CeO<sub>2</sub> phase, the CNT-free catalysts exhibited higher initial CO conversion rates. However, because of the absence of the MWCNT scaffold, the system paid a high price in terms of stability, with rapid deactivation already at low operational temperature (200 °C).<sup>103</sup>

The template effect and the possibility of removing most of the carbon are powerful tools for the design of metal-based materials with restricted morphology. The geometrical characteristics are expected to play a pivotal role in many catalytic processes, in particular the possibility to create hollow architectures. However, there are only a few reports on the exploitation of this synthetic strategy, and we believe that this line of research deserves more attention.

## Conclusions

The direct use of CNTs as all-carbon catalysts has been shown to be viable for several processes of industrial interest, and they are emerging as intriguing alternatives to metal-based catalysts, with much higher economical value. Moreover, the scope of reactions has considerably expanded over the past year. This field is relatively young and we believe it could be established as one of the predominant uses of CNTs.

CNTs could replace amorphous carbon as all-carbon catalysts, as long as a series of limitations currently hampering their use are overcome. Above all, the cost for the large-scale production of CNTs, in particular SWCNTs, is slowing down their full breakthrough at the industrial level, although much progress has been made to improve preparative protocols.

Combination of CNTs with inorganic species to prepare nanocomposite or nanohybrid catalysts represents a field of high hopes. Many experiments have confirmed the complex role that CNTs play in these systems, which delicately depends on the synthetic procedure utilized for the catalyst assembly. Homogeneity of the final materials is still an issue, and consequent reproducibility of the catalytic performance is at times debatable. Precise control over the assembly is a must if these catalysts are one day to be commercialized. In comparison with metal-free CNTs, hybrids or composites offer more versatility and a wider range of possible catalytic processes, although successful synthesis may be challenging. Photo- and electro-catalysis as well as standard heterogeneous catalysis are in full bloom, although future reports should better focus on particular sectors, such as energy, where the unique properties of CNTs may be fully exploited.

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