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 support 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 performances often superior to those of other carbon materials, in particular when ad hoc organic functional groups are attached prior to the catalytic screening. The range of catalytic reactions is quite wide, and it incorporates 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.

Introduction

The year 1991 marks a milestone in the timeline of what will be in the following years named "nanotechnology revolution", as it witnesses the official discovery of carbon nanotubes (CNTs).[1] The advent of this new carbon allotrope, together with the gradual unravelling of its fascinating structural and electronic properties, created a sensation among scientists, who foresaw a bright future for this carbon nanomaterial in several scientific areas, such as photovoltaics,[2-4] integrated circuits,[5] biosensors,[6] and nanomedicine.[7-9]

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 truly catalysts or (more often) 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 on the use of CNTs in catalysis (but also various other applicative fields), it can be today stated that CNTs have yet to completely fulfill the great promises that they held, and in some cases they still represent just exotic alternatives to better established nanomaterials. Several reasons account for this fact, and at present great efforts are being channelled towards the tackling of those most important limitations which are delaying CNT full breakthrough in real life devices or applications.

One key aspect to consider is the CNT high cost/performance ratio as compared to 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.[10] 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.[11] In addition, other protocols using CO as carbon feed are being optimized and they allow medium to large scale production.[12, 13]

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

Another limitation is the batch variance. It turns out that the optimum control of the CNT synthesis, particularly for large scale synthesis, to produce homogeneous materials is still not definite, and reproducibility can sometimes compromise the report of catalytic performances. The lack of precise control for perfectly homogeneous CNTs also leads to a change in the CNT characteristics at the nanoscale level. Although the 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 the nanotube growth, discrepancies at time arise in terms of metal content of the final materials. This is an important feature to take into account, often neglected in catalytic reports. Especially for virtually metal-free direct CNT catalysts, accurate evaluation of the potential residual metal is demanded, as even ppm fractions of metal can alter catalytic performances, 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 catalysts formulation at 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 potential success or failure of CNT-based systems for a wide range of catalytic applications, particularly for their implementation at industrial level.

Metal-free catalysts

Carbon nanotubes, both SWCNTs and MWCNTs, have drawn interest in their use as metal-free catalysts. It is often stated that use of pristine CNTs (p-CNTs) would be advantageous for those processes requiring electron transfer steps, as the electronic properties of the CNTs are preserved and can be exploited at full. 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 modified carbon nanotubes. One of the most critical problem associated with the use of p-CNTs is their high level of aggregation through extended π-π stacking, and therefore a more difficult liquid-phase manipulation.[14-16] Moreover, for many reactions, the as-introduced organic functional groups play a more direct role in the 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 work 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 in styrene.[17] However, despite the nanotubes had not undergone any specific functionalization, the mechanism suggested involved oxygen functionalities, so in strict terms this catalyst 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 site is actually not dependent on the sp^2 hybridization of the graphenic framework, but rather on the robustness of the CNT scaffold.[18] This is somehow
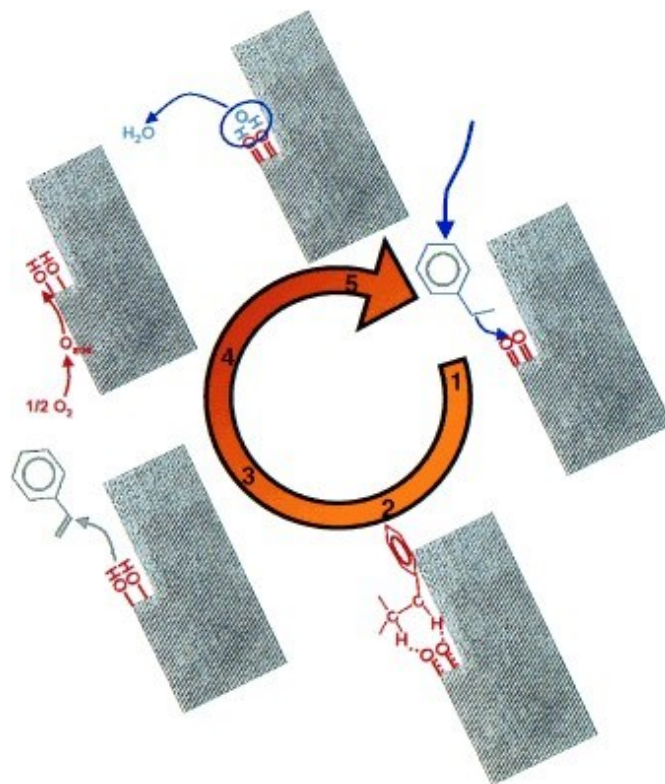

Fig. 1. Mechanism of the catalytic oxidative dehydrogenation (ODH) over carbon nanofilaments, 1) adsorption of ethylbenzene, 2) dehydrogenation at basic centers, 3) desorption of styrene, 4) adsorption of oxygen and reaction with OH groups, 5) desorption of water. Reprinted with permission from Ref.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

surprising, given the often invoked electronic properties of CNTs, and should serve as a warning that CNT catalytic behavior should not rely on common statements. 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 on the MWCNT sidewalls during the catalytic reaction, in particular with quinone/hydroxyl functional groups redox couple being the truly active sites.[19]

These and other related reports evidence a promising role for p-CNTs in 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 π-π interactions between the intermediate radical species and the CNT framework was proposed to be the key feature. As a comparison, the introduction of organic functionalities such as COOH on the CNTs did not result in any improvement in the catalytic activity, but on the contrary had an adverse effect.[20] 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.[21]

Electrocatalytic reactions. The unaltered electronic properties of p-CNTs are in theory very attractive for electrocatalytic reactions, where the good conductivity of metallic SWCNTs or MWCNTs can be advantageous for 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 by metallic SWCNTs as high as that of standard gold electrocatalysts towards the O_2 reduction (ORR). In particular, the activity was enhanced at strained sites formed during oxidation treatment by oxygen plasma etching.[22] 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 of the fill factor of DSCs.[23]

Doping and purity of CNT catalysts

An important possibility arises from the doping, in particular with nitrogen and boron, which allows a fine-tuning of the electronic properties.[24] Noteworthy, pyrolysis of iron(II) phthalocyanine in presence of NH_3 vapours and subsequent removal of residual Fe afforded vertically aligned N-doped CNTs which could be used in the electrocatalytic ORR with performances superior to those of a commercially available platinum-based electrode.[25] In another comparative study, N-doped MWCNTs and p-MWCNTs both display good activity towards the ORR, with the former proceeding through an efficient four-electron process in the alkaline condition and the latter through a two-electron process (Fig. 2).[26]

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.[27] 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.[28]

One issue that is sometimes neglected, in particular when reporting p-CNT catalysts is their actual level of purity. The most typical protocols for CNTs 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 are imperative to rule out any possible intervention of the metal into the catalytic reaction. Unfortunately, several literature reports lack a rigorous characterization study and the p-MWCNTs reported activity 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 sp^2 system and lowering of the Van
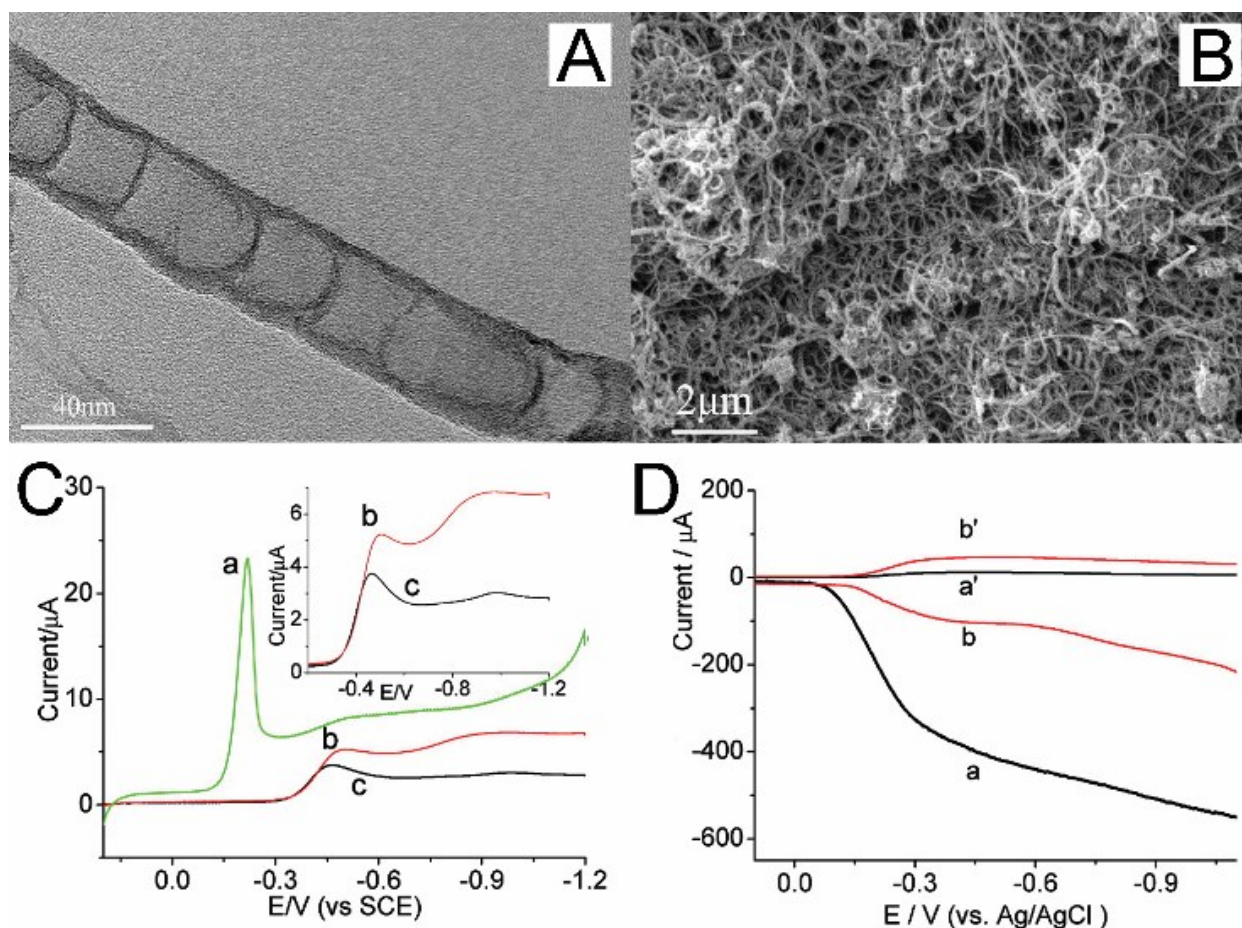
Fig. 2. TEM **(A)** and SEM **(B)** images of N-doped CNTs (NCNT). **(C)** LSV for the ORR at (a) NCNT/GC, (b) MWCNT/GC and (c) bare GC electrodes recorded in an air-saturated 0.1 M KOH solution at room temperature. Scan rate, 100 mV/s. **(D)** Steady-state voltammograms for NCNTs (curve a and a') and MWCNTs (curve b and b') at rotating ring-disk electrode in air saturated 0.1 M KOH electrolyte. Reprinted with permission from Ref. 26. Copyright © 2010 American Chemical Society.

der Waals forces responsible for the bundling.[29-31] Moreover, the as-introduced functional groups may play a key role into the specific catalysis.

Oxidation is the most employed pre-modification of CNTs, which has the double function of introducing a range of functionalities such as carboxylic acid, hydroxyls, epoxides while simultaneously purify the carbon materials by the residual metallic catalysts remained entrapped during the production step.[32] According to the oxidative protocol, a different distribution of oxygenated groups are introduced, as well as a different distribution of defects. An important advance for the utilization of o-CNTs would be to precisely control the distribution of the various oxygenated group, or even better to selectively attach single functionalities. As for 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 typically ranges in the 410–420 kJ mol^{-1}, becomes a feasible process. In a famous report, CNTs oxidized by simple reflux in HNO$_3$ exhibited high activity towards ODH of the very poorly reactive butane.[33]

Differently oxidized CNTs displayed clear differences in the electrocatalytic hydrogen peroxide reduction and oxidation, a fact related to the diverse structures of the o-CNTs, in particular the lengths and widths, obtained after the specific oxidation protocol.[34] In alternative to the common strong acid treatment, protocols based on reaction with ozone represent an interesting alternative. In a recent study, each oxygenated functional group (including COOH, OH, 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.[35] 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.[36]

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 H$_2$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.[37] Multi-step reaction schemes are in other cases required, such as in the assembly of amine-functionalized CNTs, which were proven to be suitable in the ring opening polymerization of L-proline N-carboxy anhydride (LPNCA, Fig.3). In this case, however, the f-MWCNTs only acted as radical initiator, and the polymers remain grafted onto the CNT surface.[38]

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 establishment 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 a more favourable mesoporosity as compared to the microporosity of AC that allows a more facile diffusion of the reactants to the catalytic site. Moreover, upon a well-controlled synthesis of CNTs, it is possible to have a more defined distribution of defects, 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 is assessable, replacement of metal-based catalysts with nanostructured carbon is a prospect of even higher remarkability.

ODH is a classic example of successful organic transformation, but it is not unrealistic to imagine more sophisticated transformations based on carbon backbone rearrangements, C-C or C-X (X=heteroatom) new bond formation, driven inter-
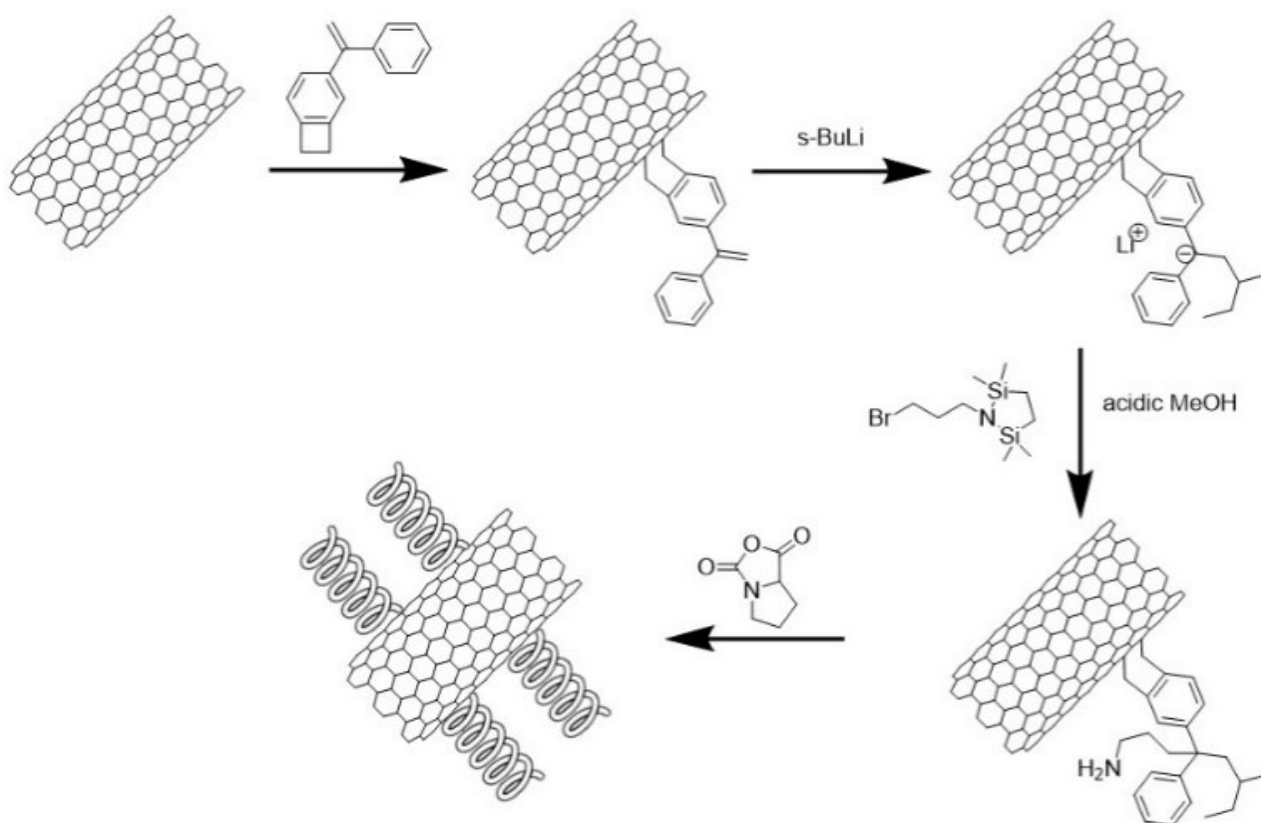

Fig. 3. Synthesis of the amino functionalized CNTs followed by surface initiated ring-opening polymerization of LP-NCA.[38]

or intra-molecular nucleophilic/electrophilic attacks etc where the use of appropriately treated CNTs 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 material of inadequate purity, while more refined techniques afford materials with high purity but in 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-π, π-π stacking and Van der Waals forces. These non-covalent molecules can help dispersing the CNTs in liquid media while leaving the polyaromatic pattern unaltered and can be in principle used as catalytic sites. However,

desorption of the molecules during reaction and consequent rapid loss of activity poses a big limitation, and therefore this route has been much less investigated for catalytic applications. Moreover, covalent modification has been associated with a decrease of toxicity of CNTs, whereas pristine materials are considered to bring much more pronounced adverse health effects.[39, 40]

Hybrids and nanocomposites

A more common utilization of CNTs in catalysis is based on their integration with inorganic phases. The resulting material is called composite or hybrid, depending on whether the inorganic and organic phases are dispersed one into each other, thus obtaining a simple addition of the properties of the two components (composite), or the two phases are interfaced in such a manner as to obtain a material with totally new properties not necessarily related to the two original components (hybrid). The number of reports on CNT nanohybrids or nanocomposites is countless and the range of applicative fields very wide. It turns out that CNTs can bring beneficial effects not only as physical supports, but also by electronic crosstalk with the catalytically active species, thus resulting in higher performances.[41] 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$_x$/CNTs). Synthetic strategies rely on *in-situ* or *ex-situ* methods. The former indicates the assembly of the inorganic compounds directly on the pristine (or modified) CNTs, while the latter refers to preformed metal nanoparticles, oxides or molecular complex that are attached to the nanocarbon supports by covalent or non-covalent bonding or by electrostatic force. A special class of composites or hybrids include the combination of three or more building blocks, to form materials in a hierarchical order that exhibit improved properties. We refer to these materials as hierarchical systems and we will provide a very restricted account of them at the end of the section.

Molecular catalysts

Functionalization of CNTs for anchoring molecular catalysts for catalysis. The most typical strategy to attach a molecular entity to the 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 by electrostatic interaction. These systems are an interesting class as they retain many of the advantages of the homogeneous molecular catalyst while bringing it into a heterogeneous phase, therefore allowing recyclability of the catalyst. 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 RhCl(PPh)$_3$ complex was attached to o-SWCNTs by means of the carboxyl acid moieties and was successfully tested in the hydrogenation of cyclohexene at room temperature.[42] However, it has been pointed 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 radical chain mechanism using a mercapto-modified SWCNT (Fig. 4).[43]

In a recent report, a rhodium complex has been 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 α-acetamidocinnamic acid.[44]

A number of other complexes have been 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 CNTs/molecular catalysts is only limited by creativity, although it has to be reminded that classic organic and organometallic chemistry on CNTs seems to suffer yet by limitations determined by the inherent CNTs structural characteristics. Reactions proceed often uncontrolled or with more difficulty and it is not always possible to use that subtlety required by coordination chemistry for metal complexes formation. However, with the progress of the "know-how" for the modification of CNTs, coupled with a more in-depth theoretical knowledge, we foresee that more and more systems with specific catalytic functions will rapidly become available.

H$_2$ production. Another actively sought field of application is the energy sector, where enormous progresses have been made in the last few years. Over the last decade, H$_2$ production is becoming one of the most explored catalytic processes, given the great appeal of H$_2$ as a new environmental-friendly energy vector. By equipping a
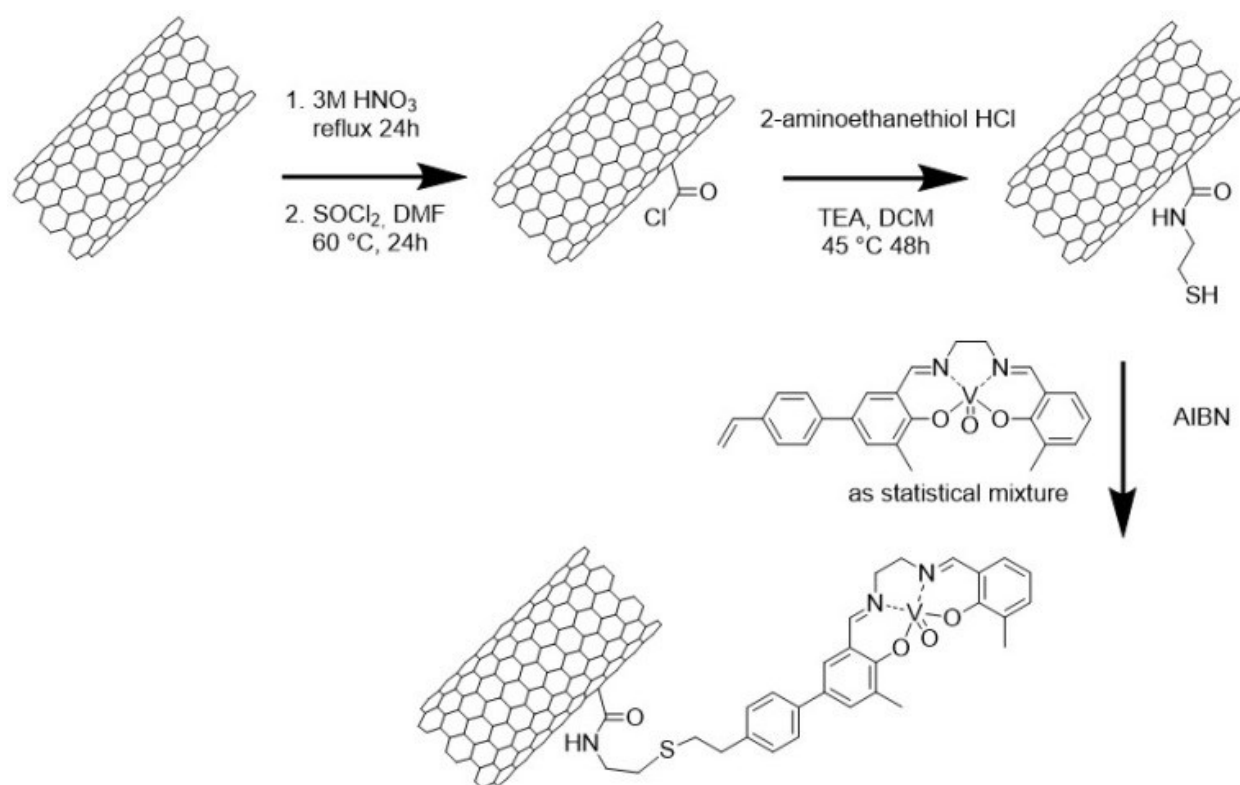
Fig. 4. Functoinalization of oxidized CNTs with a vanadyl catalyst.[43]

bioinspired Ni bisdiphosphine complex with a pendant pyrene moiety, it was possible to non-covalently adsorb such metal species on the pristine MWCNTs sidewalls through π-stacking. The adsorption proved to be robust enough to sustain electrocatalytic activation for the water reduction to produce hydrogen, with performances comparable to those of platinum catalysts, but with the extra advantage of being CO tolerant.[45] It is worth noticing that in a previous work, the authors had used a covalently modified MWCNTs 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 π-stacking strategy, a monolayer of the nickel complex could be formed, allowing a fine-tuning of the electrode characteristics. This fact introduces a fundamental problem with regards 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 CNTs 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 on the exact nature of the bond. However, whenever possible, a set of other advanced characterization techniques can supply the essential structural information.

Other than π-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 based on attachment of a Ru polyoxometalate (Ru$_4$POM) onto conductive MWCNTs. The assembly of the oxygen-evolving catalyst made use of the polyanionic nature of the Ru$_4$POM, which could be electrostatically bound to positively charged MWCNTs. The latter, in turn, were accessed through decoration with protonated polyamidoamine (PAMAM) ammonium dendrimers.[46] 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 electro-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 binding of molecular catalysts through pyrene pendants was also exploited for water oxidation reaction, by constructing a CNTs/molecular catalyst featuring the complex Ru(bpa)(pic)$_2$ (i.e. 2,2-bipyridine-6,6-dicarboxylic acid, H$_2$bpa; 4-picoline, pic) able to perform water oxidation with reported TOFs exceeding 1,700 cycles/h (Fig. 5).[47]

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 performances and high selectivity in the electroreduction of CO_2 to formate (Fig. 6).[48] CO_2 reduction is indeed becoming another crucial reaction from an environmental point of view, in line with ever more stringent regulations on CO_2 emission in the atmosphere.

General considerations and future prospects. In the vast majority of cases it seems that the CNTs exclusively have the role of physical supports. The same considerations made for the metal-free CNTs catalysts as regards to both purity and cost of CNTs apply here. 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 products, especially in the case of fine chemicals or pharmaceutical compounds. In addition, given the cost of CNTs in comparison with 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 π-systems still lacks a full understanding by means of mechanistic studies. It is envisioned that major benefits could be obtained if such relationship is more comprehensively understood.
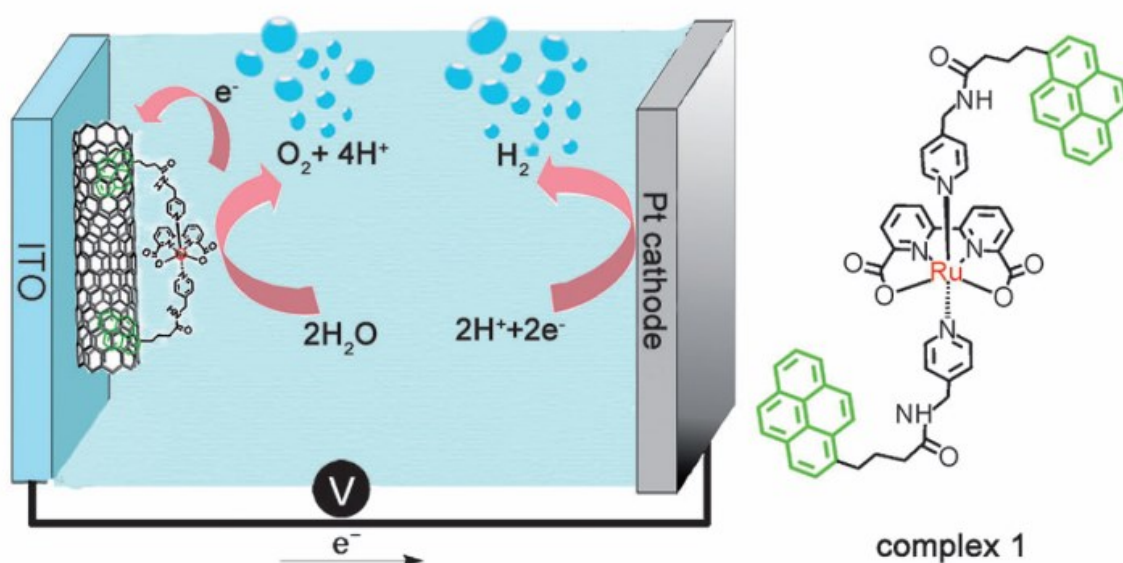

Fig. 5. Non-covalent interactions mediate the binding of Ru(bpa)(pic)$_2$ (i.e., complex 1) to CNTs for efficient electrocatalysis of water splitting. Reprinted with permission from Ref. 47, Copyright © 2011 Wiley-VCH.
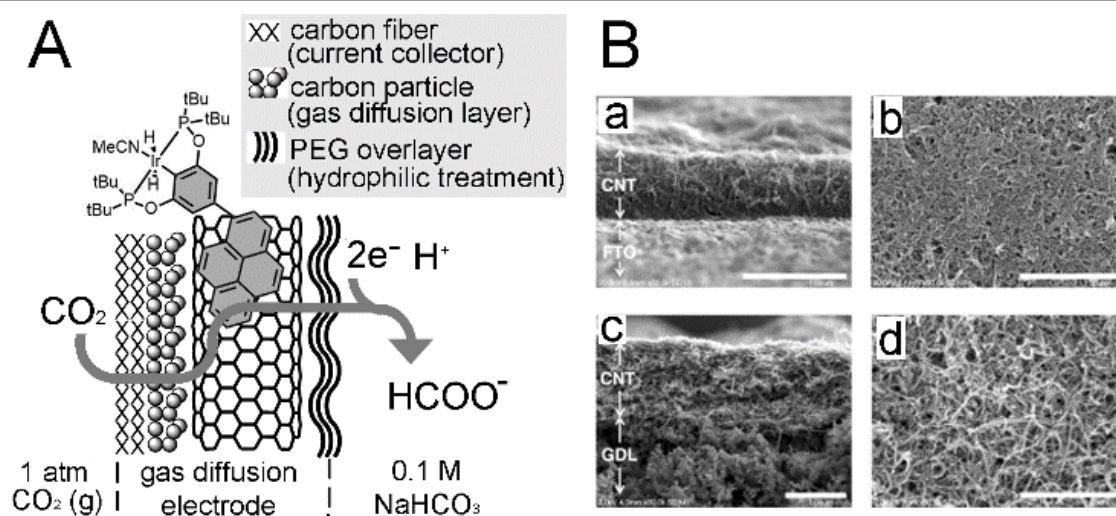

Fig. 6. (A) Scheme of the molecular catalyst/carbon nanotube-coated gas diffusion electrode for electrochemical reduction of CO2 to formate; (B) SEM images of the catalyst thin films on FTO (a, b) and GDL (c, d). Left (a,c): cross-section; right (b, d): top view. Adapted with permission from Ref. 48, Copyright © 2014 Wiley-VCH.

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 to the identification of general research trends and pinpoint some representative examples.

Hydrogenations. Hydrogenations of organic substrates are amongst the most investigated reactions featuring catalysts based on Ru, Pd, Pt, Au, Rh deposited on CNTs. Cynnamaldehyde has served as a model molecule for hydrogenations to evaluate the activity and selectivity of the catalyst. Ru/CNTs are effective to reduce cynnamaldehyde to cinnamyl alcohol[49, 50] or hydrocinnamaldehyde[51] depending on the catalyst preparation method, confirming the delicate relationship structure/activity. The same consideration on activity and selectivity applies to systems featuring Pd[52] and Pt[53] as metal active species. Similarly, reduction of nitrobenzene is a good probe reaction to evaluate the hydrogenation potential of the catalyst. This reduction has been attained with various metal nanoparticles deposited on CNTs with a series of methods.[54-56] Many other substrates have been successfully reduced by CNTs/noble metal nanocomposites and it appears that in many cases the good dispersion of the MNs onto the CNTs 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 monodispersivity). Further studies are needed to fully understand the metal–support interaction in these f-CNTs in order to improve metal nanoparticles adhesion, promote electronic interaction, as well as prevent their leaching during reaction.

Oxidations. Oxidations represent 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 screened using 2 nm Ru nanoparticles deposited on CNTs by impregnation/reduction method. These hybrids turned out to be considerably more active than the corresponding Ru nanoparticles deposited on TiO_2 or AC, with TOF of 178 h^{-1}.[57] Similarly, Au NPs deposited on o-CNTs turned out to be more active than Au NPs deposited on other supports such as Al_2O_3, SiO_2, graphite, MgO, etc. in the oxidation of cellobiose to gluconic acid.[58]

As for the CNTs/molecular catalysts, the function of the CNTs is primarily that of support, providing good dispersion and stabilizing the NPs towards aggregation/sintering. However, many studies have indicated that there may be an electronic communication between the NPs and the carbonaceous framework. Shanahan *et al.* supported Au NPs on SWCNTs and used them in the oxidation of secondary alcohol with a 95% efficiency; by UV-Vis absorption experiments they related the high activity to an electron transfer from the Au NPs to the SWCNTs.[59] Given the vast efforts devoted to the assembly of MN/CNTs, we believe that time is now mature to dedicate future studies to a higher level of fine-tuning of the deposited metal nanoparticles. For example, engineering specific crystal facets 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 hydrogenations. 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.[60]

C-C coupling reactions. Thus far, a particularly fertile soil with Pd/CNTs nanocomposites has been found in the class of C-C coupling reactions. Indeed, typical Suzuki, Sonogashira and Heck couplings have been conducted with a decent degree of success. Suzuki coupling of phenylboronic acid and 1-iodo-4-nitrobenzene to nitro-biphenyl was attained with 94% conversion after 30 min and with a TOF of 709 h^{-1}.[61] The report is particularly interesting because of the simple method of preparation of the catalyst based on supercritical CO_2 which was reported earlier by the same authors.[62] The aspect of the preparative method needs to be thoroughly considered, as it can lead to dissimilar activities deriving from different particle sizes, different metal dispersions and other features. This was demonstrated by Corma *et al.* who evaluated the Suzuki coupling of phenyl boronic acid and iodobenzene by 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.[63] For these reactions, great attention must be paid to exclude contribution of homogeneous reaction by slow metal leaching.

Better performances for the Heck reaction by Pd/CNTs catalyst as compared to Pd/C were also found for the coupling between 4-iodoanisole and styrene.[64] Similarly, several Sonogashira couplings were reported, including Pd/CNTs catalysts working under "eco-friendly" copper-free conditions and that could be efficiently recycled.[65, 66]

Electrocatalytic reactions. As for the metal-free CNTs catalysts, one very important field of applications is electrocatalysis. In particular, assembly of MN/CNT-based electrodes for fuel cells has been very much explored. In many cases the presence of CNTs leads to improved performances of the electrode, as a consequence of the excellent conduction properties of the graphenic framework and because they allow a better tailoring of the electrode surface. ORR is a classic process studied with these systems and many examples are available. Most systems are based on Pt, on accounts of the high activity of Pt towards ORR. For instance, higher rate constants for ORR were achieved on a Pt/SWCNTs-based electrode than the corresponding Pt/C electrode. Key to this finding was the high porosity of the

SWCNTs, that allowed a more facile diffusion of the reactants, and the increased electrode stability caused by the SWCNTs.[67]

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

An environmental 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 NP. This
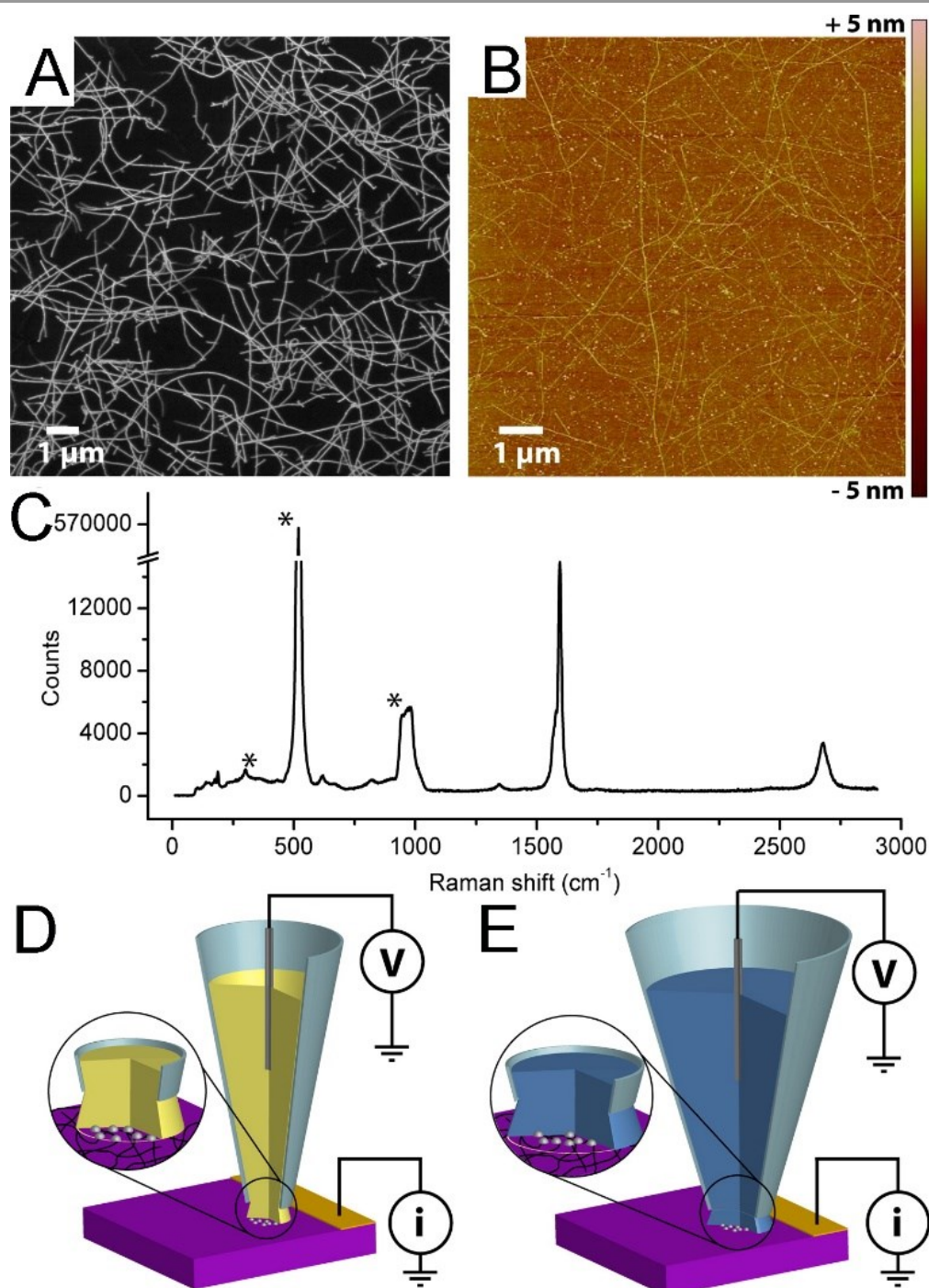

Fig. 7. E-SEM (a) and AFM (b) image of electrodeposited Pt NPs on SWCNTSa and (c) corresponding micro-Raman spectrum. Peaks marked with an * are related to the Si/SiO2 substrate. (d) Schematic of Pt NP electrodeposition using the MCEM. (e) Schematic of the set-up used to measure ORR and MOR.Reprinted from Ref. 68, Copyright © 2014, with permission from Elsevier.

approach avoids agglomeration and results in longer term operational stabilities for methanol oxidation by the assembled electrode.[69]

Despite the large number of Pt/CNTs 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_3C NP hybrids by annealing a mixture of melamine, PEG-PPG-PEG Pluronic P123, and $Fe(NO_3)_3$. The resulting material exhibited a half-wave potential of 0.861 V for ORR, almost 50mV more positive than that of 20 wt% Pt/C catalyst.[70] 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 CNTs channels appears to be more promising (see next section). Alloys of 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 tested for ORR and methanol oxidation reaction (Fig. 8). The ternary metal catalysts exhibited the 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.[71]
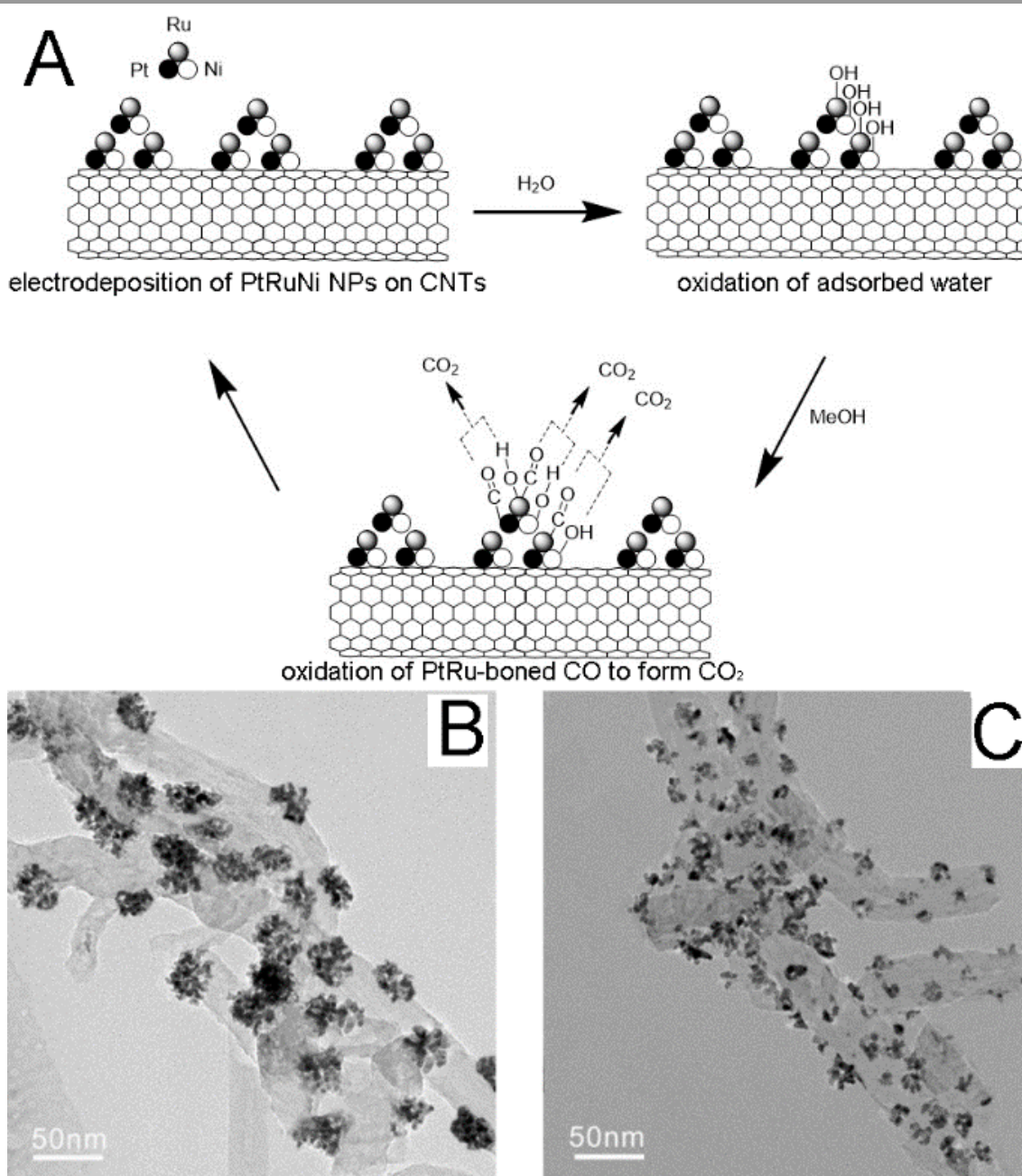
Fig. 8. A. Scheme for mechanism for PtRuNi/MWCNTs electrode surface in the methanol solution. **B,C.** TEM images of **(B)** PtRu (8:2)/MWCNTs and **(C)** PtRuNi (8:1:1)/MWCNTs catalysts. Adapted from Ref. 71 with permission from Elsevier, Copyright (2014).

Other reactions. Coimpregnation method has also been used to support other bimetallic nanoparticles on CNTs, such as the catalyst RuFe/CNTs, which was active in the hydrogenolysis of glycerol to 1,2-propanediol and ethylene glycol. A comparison with the correspondent monometallic Ru/CNTs demonstrated a more pronounced efficiency of the bimetallic system towards the C-O breakage, resulting in higher selectivity towards glycol products, whereas the monometallic favours C-C cleavage, thus leading to large amounts of CH_4.[72]

General considerations and future prospects. In general terms, as compared to molecular catalysts, MNs deposited onto CNTs have enjoyed so far an even higher popularity, mostly on accounts 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 reaction is broad. Hydrogenation and oxidation reactions keep proliferating and the scope of reactions is becoming 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 construction of fine chemicals, for example in the multistep synthesis of complex biomolecules. On the other hand, the electrocatalysis field is approaching a level that goes beyond fundamental studies, and design of electrodes from an engineer point of view, namely for real fuel cells construction, seems to be well within reach.

Metal oxides

TiO₂/CNT catalytic systems. A large variety of CNTs/metal oxides has been synthesised for catalytic purposes using a range of procedures. One of the most investigated systems has been TiO_2/CNTs. The well-known photocatalytic properties of the semiconductor TiO_2 has inspired many groups in developing TiO_2/CNTs photocatalysts, which in many cases bring up improved photocatalytic performances. It is commonly accepted that the benefits of interfacing TiO_2 with CNTs are beyond a simple improved structural stability. In one proposed mechanism, the CNTs act as efficient scavengers of the photoexcited electron from the CNTs, retarding the electron/hole recombination rates by means of hetero-junctions formed at the interface with the semiconductor. Alternatively, a role of photosensitizer has been proposed, with the electron excited and injected from the CNTs into the TiO_2 conduction band, with subsequent electron transfer from the TiO_2 valence band to the CNTs, forming a charge separation state (electron/hole) on the TiO_2 (Fig. 9).[73]

Although the first mechanism is today most frequently mentioned, some reports on the photocatalytic activity under visible light (despite TiO_2 being a UV active semiconductor) serve as a warning that careful examination of several 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 TiO_2/MWCNTs prepared via a modified sol-gel method is a remarkable example of the complexity of the mechanism,
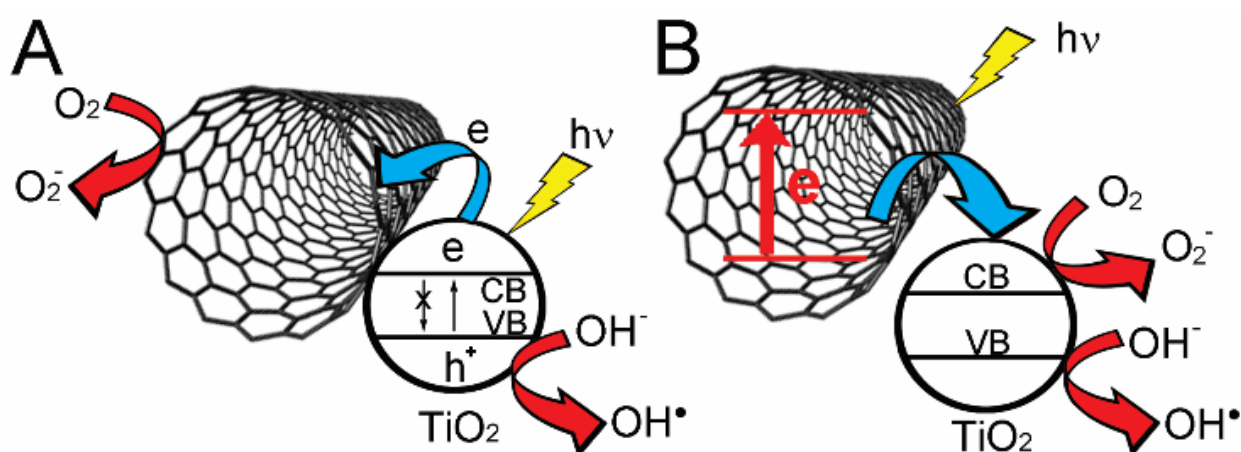

Fig. 9. The two possible functions of CNTs when hybridised with a semiconductor such as TiO_2. **(A)** electron sink and **(B)** photosensitiser.[73]

where the authors invoked photosensitizing by the CNTs.[74] However, in a report on the visible light catalytic photoelectroactivity of a TiO_2/CNTs-modified ITO electrode for the degradation of phenol, XPS investigations indicated presence of Ti-C and Ti-O-C bonds formed during calcination by substitution of oxygen and titanium atoms with C. The visible light efficiency was thus attributed to this "doping" effect, rather than to a photosensitizing role of the CNTs.[75] In conclusion, considering the large number of TiO_2/CNTs catalysts, it is apparent how further studies, perhaps involving more sophisticated techniques such as transient adsorption 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 MO_x/CNT systems.

Regardless of the exact role, however, it is clear from experimental evidence that the direct participation of the CNTs into the photocatalytic process exists. For this reason, it becomes imperative that the contact between the two phases is maximised both in terms of vicinity and of 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 deriving from the presence of CNTs are related to the maximisation of the semiconductor exposed area to the light, and therefore an optimised light absorption and increased quantum efficiency.

Most reports on TiO_2/CNTs have focused on the degradation of pollutants. Other than phenol, substrates such as methylene blue (MB),[76] methyl orange,[77] indigo carmine,[78] and many other molecules have been tested. Probably, the literature has almost reached saturation and therefore unless some exceptional performances are noted, some peculiar effects observed or visible light activity found, we feel that interest should shift towards other photoactivated processes, in particular related to energy. H_2 evolution is a potential field, so far being successfully exploited by using mainly hierarchical systems (see next section), where the TiO_2/CNTs is further modified with metal nanoparticles for enhancing activities. CO_2 photo-reduction is another important energy and environmental application. Reduction of CO_2 by TiO_2/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 TiO_2, formed according to the synthetic method used, are correlated with the selectivity towards a specific product.[79] More recently, a catalyst working under visible light was synthesised through a simple coating approach, and promising, although not excellent, activities for the photoreduction of CO_2 to methane were observed.[80]

Other MO_x/CNT catalytic systems. As a common alternative to TiO_2, another frequently employed photoactive metal oxide that has been combined with CNTs is ZnO. As for TiO_2, research in photocatalysis has mostly been devoted to the abatement of water contaminants, such as methylene blue[81] or Rhodamine B.[82] Other metal oxides have been reported as photocatalysts.

In analogy with CNTs/molecular metal catalysts and MN/CNTs, construction of electrodes with MO_x/CNTs for electro-catalytic applications has been fast developing. A poly(sodium 4-styrene sulfonate)-assisted route gave access to MnO_2/MWCNTs that exhibited moderate activity toward the four-electron reduction of oxygen in alkaline media with no further precious metal required.[83] The same process was also achieved by a catalysts prepared by growing Co_3O_4 nanocrystals on N-doped CNTs.[84] More recently, a series of MO_x (MnO_2, Co_3O_4, NiO, CuO, Fe_xO_y) loaded onto N-doped CNTs via an impregnation method resulted in activities comparable to carbon-supported Pt-based catalysts for ORR in alkaline media, as well as the oxygen evolution reaction, and dependent upon the specific morphology of the catalyst.[85] The examples demonstrate that by appropriate choice of MO_x and synthetic conditions, precious metal-free MO_x/CNTs electrodes can be assembled and successfully used for specific purposes. On the other hand, assembly of electrochemical sensors or supercapacitors based on MO_x/CNTs represent a fruitful field of research, worth further exploitation. Among others, examples with Fe_3O_4,[86] RuO_2,[87, 88] WO_3,[89] and in particular SnO_2,[90-93] have been reported.

Although photo- and electro-catalysis are predominantly explored, standard heterogeneous catalysis falls within the scope of reactions catalysed by MO_x/CNTs systems, and it is a field that merits deeper investigation. This is substantiated by several examples in literature, such as the methanol oxidation by a RuO_2/MWCNT catalyst prepared through oxidation precipitation method,[94] and the highly active and selective dehydrogenation of ethylbenzene by Fe_2O_3/CNTs.[95]

In contrast with MN/CNTs, which offer many examples in several catalytic processes, recent trends seem to address MO_x/CNTs as platforms for the assembly of more complex systems with improved performances (hierarchical systems). Apart from TiO_2/CNTs, not as many examples of direct use of MO_x/CNTs in catalysis are available as compared to MN/CNTs, although the bulk of reports is not negligible, particularly for photocatalytic applications. Synthesis of MO_x/CNTs generally implies use of higher metal oxide loadings as compared to metal nanoparticles, therefore the resulting hybrids or composites show structures where the oxide more or less uniformly envelop the CNTs. It is worth noting that the standard preparative methods in many cases lead to materials with poor homogeneity, with the presence of considerable amounts of 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/CNTs and MO_x/CNTs systems have been clearly identified, the possibility to create hybrids by combination of three (or more) building blocks elevate 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 it does the difficulty in its

preparation. However, the obstacles rising in the assembly step are often compensated by a considerable enhancement of the catalytic functionality. Most frequently, the catalysts consist of ternary systems NM/MO$_x$/CNTs.

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

As a common example, we can take the assembly of Pt/TiO$_2$/CNTs materials used in photocatalytic hydrogen evolution. The addition of Pt nanoparticles to the TiO$_2$/CNTs composites results in a very significant increase of the catalytic activity. The often invoked mechanism is based on the injection of the photo-excited electron of TiO$_2$ into the Pt orbitals, where the catalytic reduction reaction actually occurs. The consequence of this electron transfer is reduced recombination rates of the separate charges and in turn the enhancement of activity. This has been shown in a few reports on the hydrogen evolution from water solution in presence of a sacrificial electron donor.[96-98] Other less precious metals such as Ni or Pd can also be proficiently used for the purpose.[99] Solvent-free oxidation of benzyl alcohol was achieved with good selectivity using a hierarchical CNTs/MnO$_x$/Pd catalyst (Fig. 11), where the MnO$_2$ was first immobilised via impregnation on the CNTs support, followed by deposition of
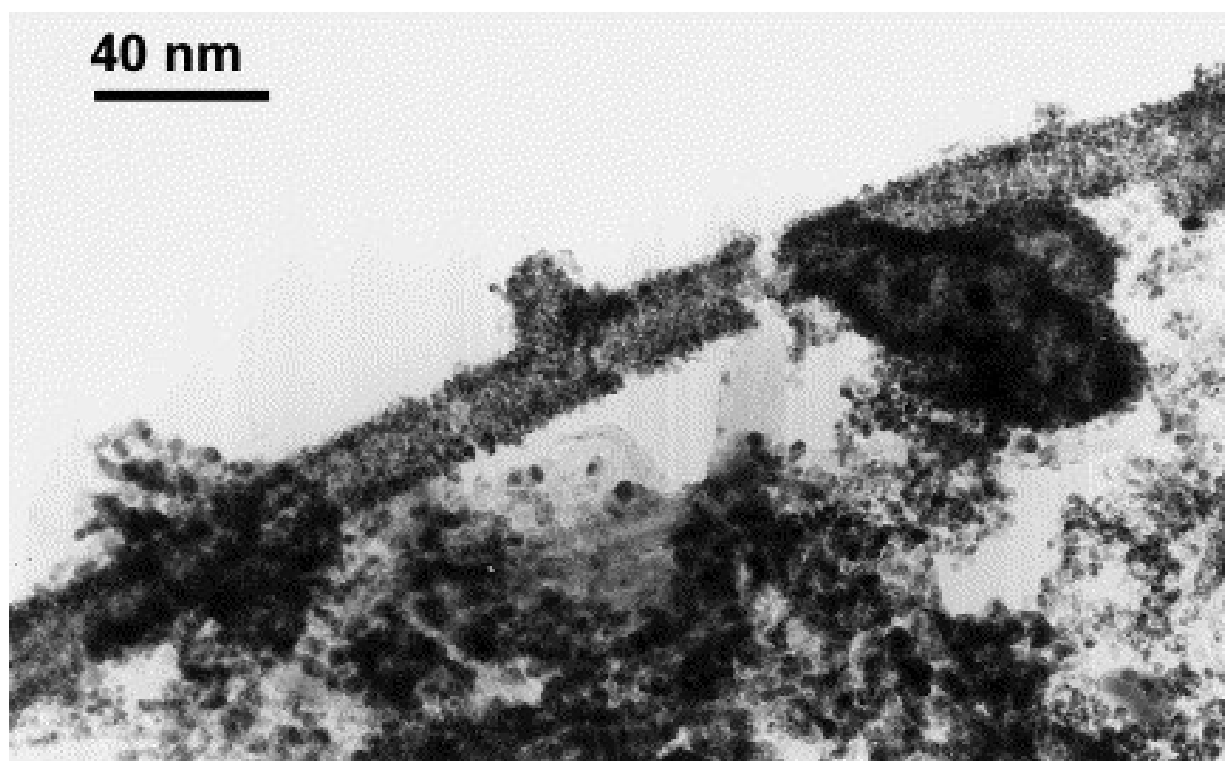

Fig. 10. TEM image of a non-homogeneous nanocomposite.[100] Reprinted from Ref. 100 with permission from Elsevier, Copyright (2002).

Pd nanoparticles. The ternary catalyst showed an improved performance attributable to a more facile electron transfer at the MnO$_x$-Pd interface and a promotion of oxygen activation through lattice oxygen transport onto the active site. The stability was excellent, due to the hybridization of the metal oxide with the CNT scaffold.[101]

Core-shell systems. In our efforts devoted to the synthesis of hierarchical hybrid systems incorporating CNTs, we have developed a sol-gel strategy where it is possible to envelop CNTs into layers of a metal oxide phase (CeO$_2$, TiO$_2$, ZrO$_2$) embedding noble metal nanoparticles (Pd, Pt). The synthesis features the pre-assembly of the binary inorganic phase into a core-shell structure (MN@MO$_x$) where the noble metal is surrounded by a metal alkoxide precursor, which is then reacted with an appropriately functionalised MWCNTs. Final controlled hydrolysis produces a hierarchical NM@MO$_x$/MWCNTs hybrid (Fig. 12). We have proven that the structure of the hybrid, with the core-shell hierarchy of the inorganic matrix, results into an improved stability of the system, which is also reflected into a higher activity. The catalyst bears a 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.[102]

We also recently demonstrated how the system may be further improved for the specific process by means of thermal treatments, and how the homogeneity of the catalyst, which depends on the relative composition, is an essential parameter to consider during the catalyst formulation phase.[103]

The NM@MO$_x$ 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 on Ni@NiO/CNT. The authors ingeniously exploited the CNT 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 the NiO and the CNTs that impede complete reduction, is key to the outstanding activity.[104]
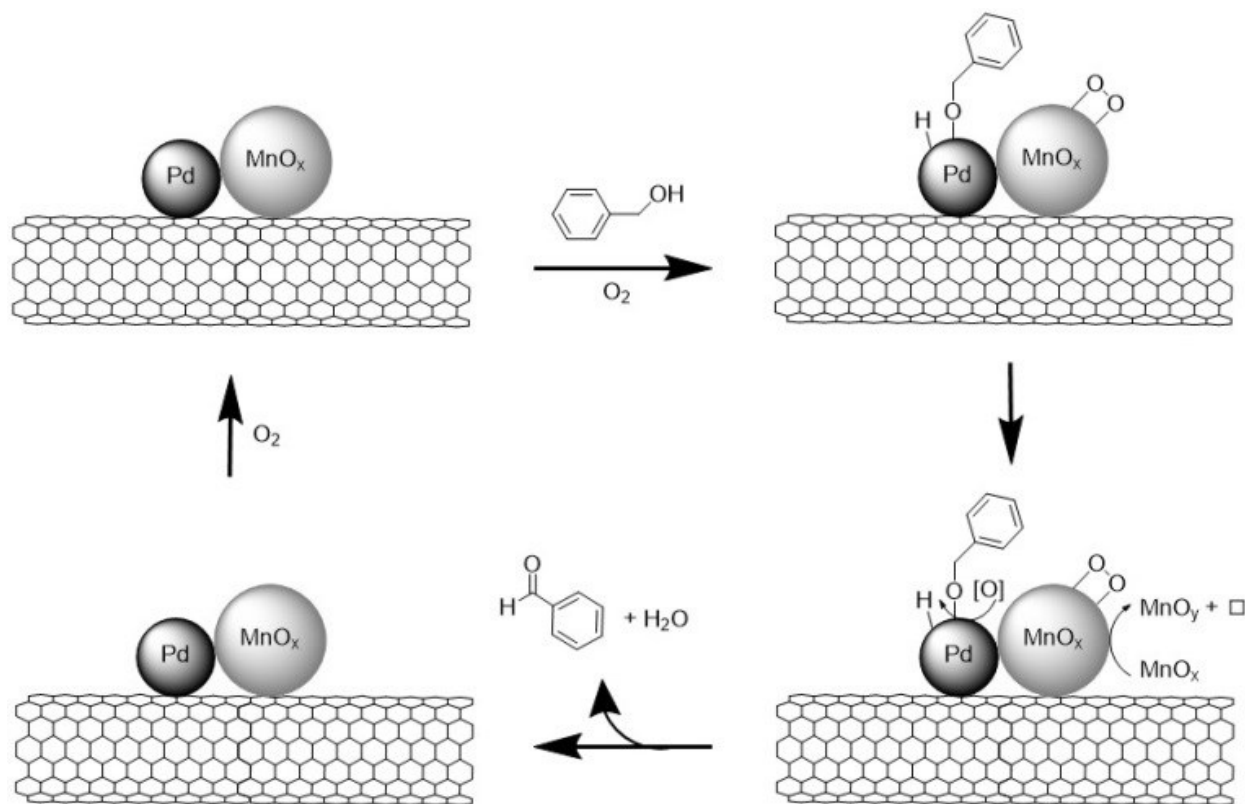

Fig. 11. Solvent-free oxidation of benzyl alcohol was achieved with good selectivity using a hierarchical CNTs/MnO$_x$/Pd catalyst.[101]
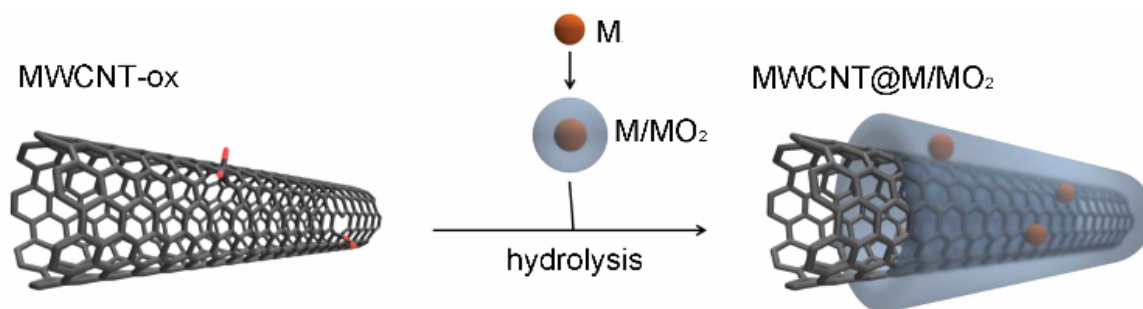

Fig. 12. Synthesis of core-shell systems features the pre-assembly of the binary inorganic phase into a core-shell structure where the noble metal (M) is surrounded by a metal alkoxide precursor, which is then reacted with an appropriately functionalised MWCNTs. Final controlled hydrolysis produces a hierarchical MWCNT@M/MO$_2$ hybrid. Reprinted with permission from Ref. 102. Copyright © 2012 American Chemical Society.

Considerations on hierarchical systems. From the above examples, it is obvious that switching to ternary (or more) 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 as-assembled architecture is carefully designed in order to exhibit defined functionality.

Confined space

Role of CNTs in catalysis

An intriguing possibility arising with CNTs and that cannot be offered by most of other carbon nanostructures is the endohedral filling with catalytically active species that has been known for more than a decade.[105] Indeed, the inner cavity of CNTs can be subjected to modification with other entities to produce what is sometimes referred to as *confinement effect*.[106] The definition aims at explaining the different behaviour of compounds deposited outside or inside CNTs. As a representative example, two hybrids with Pt nanoparticles deposited respectively inside the MWCNT channel or outside were prepared and tested for the asymmetric hydrogenation of ethyl pyruvate in presence of cinchonidine as chiral modifier. It turned out that the former catalyst could reach TOF as high as 100000 h^{-1} and 96% ee, as opposed to the 15000 h^{-1} and 75% ee of the latter.[107]

Several aspects have been examined, such as the higher π-electron density on the outer layer of MWCNTs due to the graphene curvature, as shown by TPR, CO adsorption microcalometry, and first principles calculations on Ru nanoparticles deposited in the interior or the exterior of CNTs.[108] An enhanced pressure of the reactants in nanosized channels has also been proposed.[109] Two more explanations could be related to a diminished agglomeration tendency of the metal catalysts in the confined space as compared to the outer particles[110] and an increase of turnover numbers as a consequence of a higher frequency of adsorption of reactant molecules. However, this latter hypothesis is weakened by considering the restriction posed by the nanotubes walls to the free in/out transfers 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 upon 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, Li appear to be beneficial in the ethanol generation from syngas (Fig. 13),[111] outer Ru nanoparticles are more efficient in the ammonia decomposition than the internalised ones.[112]

In any case, findings on CNTs 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 Suzuki have been reported in water, with the embedded Pd nanoparticles showing a much higher resistance towards sintering.[113] This might spark interest in those groups interested in industrial relevant processes. The decomposition of ammonia to produce H_2 proved to be a useful test reaction, particularly benefiting from the structural features of the nanohybrids, and other than with Ru, it has been proved to be achievable also with more cost-effective CNT-encapsulated bimetallic particles, such as Fe-Co alloys (Fig. 14).[114]
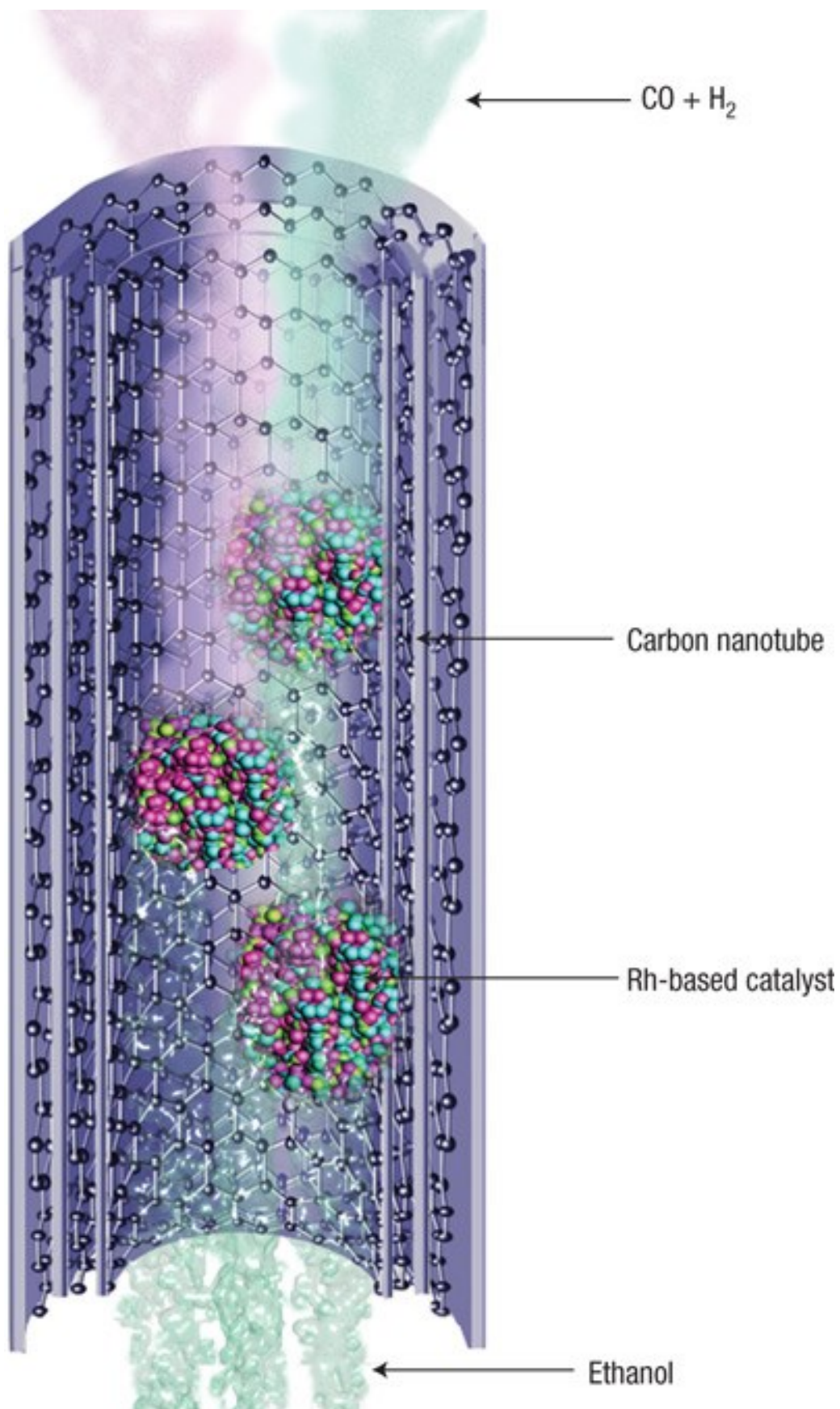
Fig. 13. Schematic diagram showing ethanol production from syngas inside Rh-loaded carbon nanotubes. Reprinted by permission from Macmillan Publishers Ltd.: Ref. 111. Copyright © 2007.
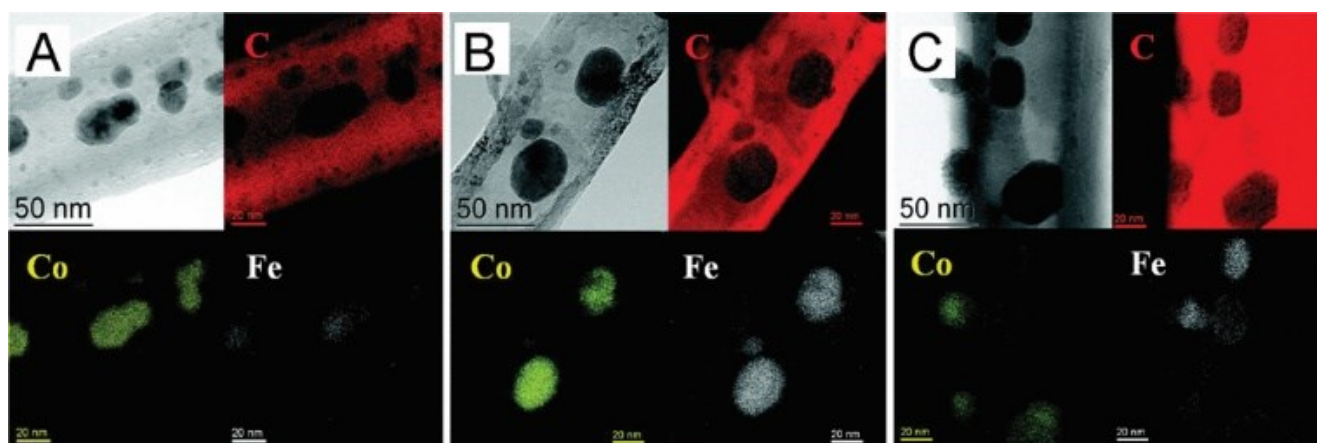
Fig. 14. Electron Energy Loss Spectroscopy (EELS) elemental mappings of fresh samples: (A) 5% Co$_2$Fe/CNTs, (B) 5% CoFe/CNTs, and (C) 5% CoFe$_5$/CNTs. Adapted with permission from Ref. 114. Copyright © 2008 American Chemical Society.

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 hydrogenations could be a more favourable prospect, because of the unique properties of the nanochannels. Very recently, a 96% ee and TOF as high as 105 h^{-1} were reported for the asymmetric hydrogenation of α-chetoesters by a catalyst comprising endohedral Pt nanoparticles/CNTs in the presence of cinchonidine as chiral modifier.[107]

The function of the CNTs could be not only that of nanoreactor, but it could also relate to an active participation into 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 an across-layer electron transfer from metal Fe to the outer CNT layer it has been possible to carry out electrocatalytic ORR in acidic media at the external CNT surface. In this case, other than acting as electron shuttle, the CNTs scaffold provides protection for the Fe towards leaching. The finding is of relevance for the development of new electrodes for polymer electrolyte membrane fuel cells (PEMFC).[115] We extended this work, and recently discovered that functionalization of the outer shell of Fe@MWCNTs with benzoic acid groups through radical addition from diazonium salt intermediates results in a catalyst capable of activating both ORR and HER under physiological conditions.[116]

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 CNTs channels, using for example the classic microcapillarity method[117, 118] is not trivial and it often leads to non-uniform materials, with metal outside the CNTs that needs to be removed. In alternative, it appears that *in situ* methods, namely encapsulation of the metal during the production phase of the CNT, are a promising strategy that has greatly progressed, but it still requires better control.[119] Internalization of 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 could have a defined impact in the 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 the purpose. In a classic example, surface tension effects drove the growth of crystalline V$_2$O$_5$ oxide 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 V$_2$O$_5$ fibres with desired widths.[120]

A variety of metal oxides has 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 the 1D growth is initiated, the oxide is capable of continuing the growth along the preferential longitudinal direction.[121]

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 it has been demonstrated in the CO oxidation by hollow CeO_2 nanotubes prepared using CNTs as removable templates. Other than an impact given by the 1D architecture, it turned out that the improvement in activity performance was also to be attributed to the remains of the CNTs after thermal treatment, as they act as dopant forming $CeO_{2-x}C_x$ species, bearing Ce^{3+} atoms (Fig. 15).[122]
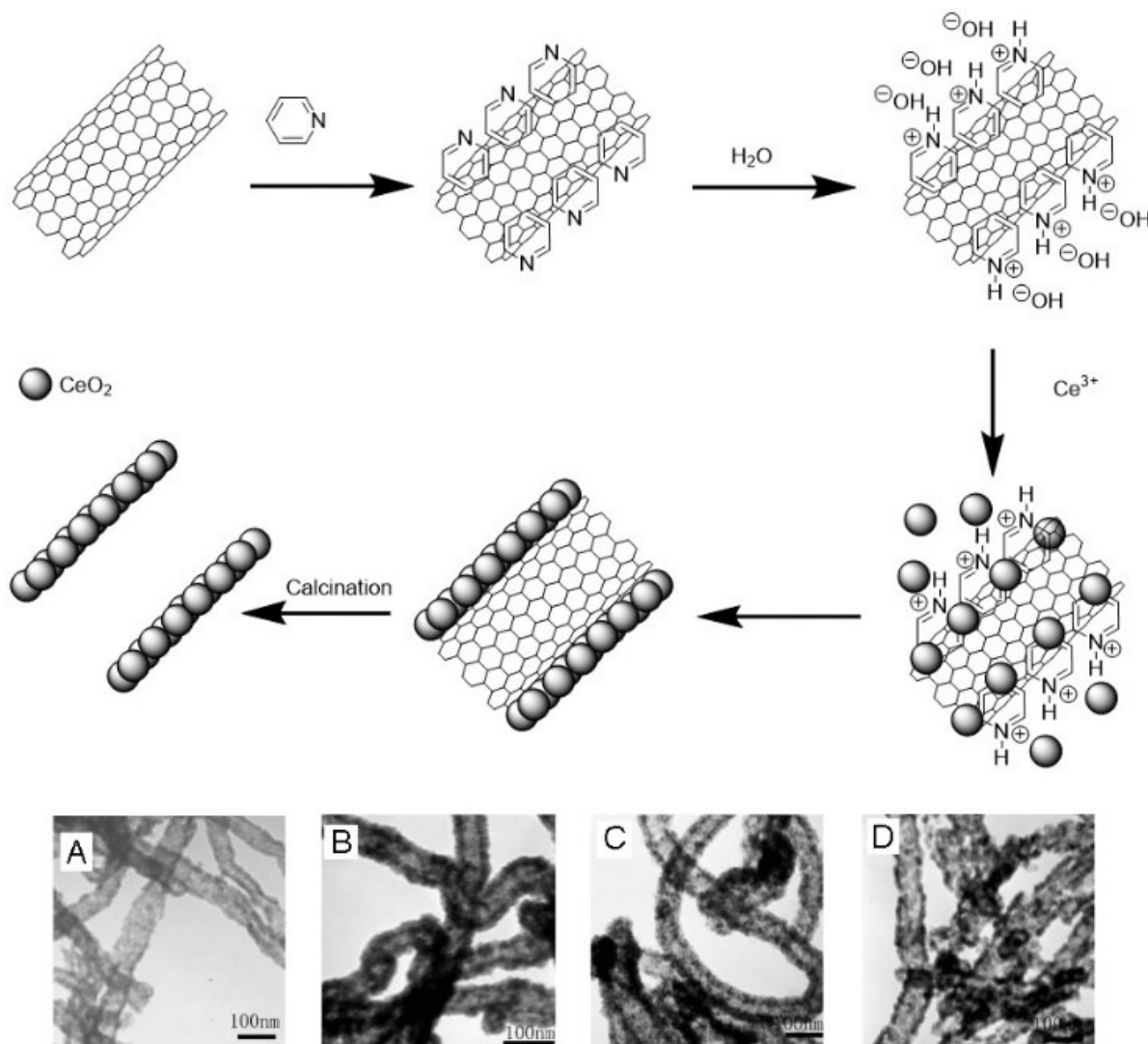

Fig. 15. Proposed mechanism for the formation of CeO_2 nanotubes (top). TEM images of CeO_2 nanotubes calcined for 30 min. at A) 450 °C, B) 500 °C, C) 550 °C, and D) 600 °C for 10 h. Adapted from Ref. 122 with permission from Elsevier. Copyright © 2008.

However, in most cases removal of the CNTs appears to be detrimental. We evaluated the water-gas shift reaction using different compositions of $Pd@CeO_2/MWCNTs$ 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 the higher calcination brought higher crystallinity of the CeO_2 phase, the CNT-free catalysts exhibited higher initial CO conversion rate. 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).[103]

The template effect and the possibility of removing most of the carbon is a powerful tool 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 given the possibility to create hollow architectures. However, the reports on the exploitation of this synthetic strategy are only a few, and we believe that this branch of research deserves more attention.

Conclusions

Direct use of CNTs as all-carbon catalysts has been shown to be viable for several processes of industrial interest, and it is emerging as an intriguing alternative to metal-based catalysts, of much higher economical value. Moreover, the scope of reactions has been considerably expanding over the last year. The field is relatively young and we believe it could establish itself as one of the predominant use of CNTs.

CNTs could replace amorphous carbon as all-carbon catalysts, as long as a series of limitations currently hampering their use is overcome. Above all, the cost for the large-scale production of CNTs, in particular SWCNTs, is slowing down the full breakthrough at industrial level, although many progresses are being 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 be better focused on particular sectors, such as energy, where the unique properties of CNTs may be fully exploited.

Acknowledgements

Notes and references

1. S. Iijima, *Nature*, 1991, **354**, 56-58.
2. L. Dai, D. W. Chang, J.-B. Baek and W. Lu, *Small*, 2012, **8**, 1130-1166.
3. S. Cataldo, P. Salice, E. Menna and B. Pignataro, *Energy Environ. Sci.*, 2012, **5**, 5919-5940.
4. A. J. Ferguson, J. L. Blackburn and N. Kopidakis, *Mater. Lett.*, 2013, **90**, 115-125.
5. J. John, E. Gravel, I. N. Namboothiri and E. Doris, *Nanotech. Rev.*, 2012, **1**, 515-539.
6. Z. Chen, X. Zhang, R. Yang, Z. Zhu, Y. Chen and W. Tan, *Nanoscale*, 2011, **3**, 1949-1956.
7. S. Marchesan, M. Melchionna and M. Prato, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2013, **22**, 190-195.
8. S. Marchesan, K. Kostarelos, A. Bianco and M. Prato, *Mater. Today*, 2015, **18**, 12-19.
9. S. Marchesan and M. Prato, *ACS Med. Chem. Lett.*, 2013, **4**, 147-149.
10. P. J. F. Harris, *Carbon Nanotube Science 2nd Ed.*, Cambridge University Press, Cambridge, UK, 2011.
11. J. P. Tessonnier, M. Becker, W. Xia, F. Girgsdies, R. Blume, L. Yao, D. S. Su, M. Muhler and R. Schlögl, *ChemCatChem*, 2010, **2**, 1559-1561.
12. J. H. Hafner, M. J. Bronikowski, B. R. Azamian, P. Nikolaev, A. G. Rinzler, D. T. Colbert, K. A. Smith and R. E. Smalley, *Chem. Phys. Lett.*, 1998, **296**, 195-202.
13. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. Smith and R. E. Smalley, *Chem. Phys. Lett.*, 1999, **313**, 91-97.
14. R. C. Haddon et al., *Acc. Chem. Res.*, 2002, **35**, 997-1113.
15. J. N. Coleman, A. Fleming, S. Maier, S. O'Flaherty, A. I. Minett, M. S. Ferreira, S. Hutzler and W. J. Blau, *J. Phys. Chem. B*, 2004, **108**, 3446-3450.
16. C. N. R. Rao, B. Satishkumar, A. Govindaraj and M. Nath, *ChemPhysChem*, 2001, **2**, 78-105.
17. G. Mestl, N. I. Maksimova, N. Keller, V. V. Roddatis and R. Schlögl, *Angew. Chem. Int. Ed.*, 2001, **40**, 2066-2068.
18. J. Zhang, X. Wang, Q. Su, L. Zhi, A. Thomas, X. Feng, D. S. Su, R. Schlögl and K. Müllen, *J. Am. Chem. Soc.*, 2009, **131**, 11296-11297.
19. X. Liu, D. S. Su and R. Schlögl, *Carbon*, 2008, **46**, 547-549.
20. J. Luo, F. Peng, H. Yu, H. Wang and W. Zheng, *ChemCatChem*, 2013, **5**, 1578-1586.
21. W. Zhang, H. Zhang, J. Xiao, Z. Zhao, M. Yu and Z. Li, *Green Chem.*, 2014, **16**, 211-220.
22. J. C. Byers, A. G. Güell and P. R. Unwin, *J. Am. Chem. Soc.*, 2014, **136**, 11252-11255.
23. S. H. Seo, S. Y. Kim, B.-K. Koo, S.-I. Cha and D. Y. Lee, *Langmuir*, 2010, **26**, 10341-10346.
24. S.-S. Yu and W.-T. Zheng, *Nanoscale*, 2010, **2**, 1069-1082.

25.   K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, *Science*, 2009, **323**, 760-764.
26.   X. Xu, S. Jiang, Z. Hu and S. Liu, *ACS Nano*, 2010, **4**, 4292-4298.
27.   H. Yu, F. Peng, J. Tan, X. Hu, H. Wang, J. Yang and W. Zheng, *Angew. Chem. Int. Ed.*, 2011, **50**, 3978-3982.
28.   B. Frank, J. Zhang, R. Blume, R. Schlögl and D. S. Su, *Angew. Chem. Int. Ed.*, 2009, **48**, 6913-6917.
29.   D. Tasis, N. Tagmatarchis, A. Bianco and M. Prato, *Chem. Rev.*, 2006, **106**, 1105-1136.
30.   G. Giambastiani, S. Cicchi, A. Giannasi, L. Luconi, A. Rossin, F. Mercuri, C. Bianchini, A. Brandi, M. Melucci and G. Ghini, *Chem. Mater.*, 2011, **23**, 1923-1938.
31.   M. Melchionna and M. Prato, in *Nanocarbon-Inorganic Hybrids   Next   Generation Composites for Sustainable Energy Applications*, 2014, DOI: 10.1515/9783110269864.43.
32.   J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov and C. B. Huffman, *Science*, 1998, **280**, 1253-1256.
33.   J. Zhang, X. Liu, R. Blume, A. Zhang, R. Schlögl and D. S. Su, *Science*, 2008, **322**, 73-77.
34.   P. Cañete-Rosales, V. Ortega, A. Álvarez-Lueje, S. Bollo, M. González, A. Ansón and M. T. Martínez, *Electrochim. Acta*, 2012, **62**, 163-171.
35.   Y. Zhang, C. Chen, L. Peng, Z. Ma, Y. Zhang, H. Xia, A. Yang, L. Wang, D. S. Su and J. Zhang, *Nano Res.*, 2015, **8**, 502-511.
36.   J. Wang, W. Fu, X. He, S. Yang and W. Zhu, *J. Environ. Sci.*, 2014, **26**, 1741-1749.
37.   Q. Shu, Q. Zhang, G. Xu and J. Wang, *Food Bioprod. Process.*, 2009, **87**, 164-170.
38.   M. Gkikas, B. P. Das, M. Tsianou, H. Iatrou and G. Sakellariou, *Eur. Polym. J.*, 2013, **49**, 3095-3103.
39.   J. Kolosnjaj, H. Szwarc and F. Moussa, *Adv. Exp. Med. Biol.*, 2007, **620**, 181-204.
40.   A. E. Porter, M. Gass, K. Muller, J. N. Skepper, P. A. Midgley and M. Welland, *Nat. Nanotechnol.*, 2007, **2**, 713-717.
41.   M. Melchionna, M. Bonchio, F. Paolucci, M. Prato and P. Fornasiero, in *Making and Exploiting Fullerenes, Graphene, and Carbon Nanotubes*, Springer, 2014, pp. 139-180.
42.   S. Banerjee and S. S. Wong, *J. Am. Chem. Soc.*, 2002, **124**, 8940-8948.
43.   C. Baleizão, B. Gigante, H. Garcia and A. Corma, *J. Catal.*, 2004, **221**, 77-84.
44.   C. C. Gheorghiu, B. F. Machado, C. Salinas-Martinez de Lecea, M. Gouygou, M. C. Roman-Martinez and P. Serp, *Dalton Trans.*, 2014, **43**, 7455-7463.
45.   P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave and V. Artero, *Angew. Chem. Int. Ed.*, 2011, **123**, 1407-1410.
46.   F. M. Toma, A. Sartorel, M. Iurlo, M. Carraro, P. Parisse, C. Maccato, S. Rapino, B. R. Gonzalez, H. Amenitsch and T. Da Ros, *Nat. Chem.*, 2010, **2**, 826-831.
47.   F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li and L. Sun, *Angew. Chem. Int. Ed.*, 2011, **50**, 12276-12279.
48.   P. Kang, S. Zhang, T. J. Meyer and M. Brookhart, *Angew. Chem. Int. Ed.*, 2014, **53**, 8709-8713.
49.   J. Planeix, N. Coustel, B. Coq, V. Brotons, P. Kumbhar, R. Dutartre, P. Geneste, P. Bernier and P. Ajayan, *J. Am. Chem. Soc.*, 1994, **116**, 7935-7936.
50.   H. Vu, F. Gonçalves, R. Philippe, E. Lamouroux, M. Corrias, Y. Kihn, D. Plee, P. Kalck and P. Serp, *J. Catal.*, 2006, **240**, 18-22.
51.   X. Ni, B. Zhang, C. Li, M. Pang, D. Su, C. T. Williams and C. Liang, *Catal. Commun.*, 2012, **24**, 65-69.
52.   J.-P. Tessonnier, L. Pesant, G. Ehret, M. J. Ledoux and C. Pham-Huu, *Appl. Catal. A: Gen.*, 2005, **288**, 203-210.
53.   Z.-T. Liu, C.-X. Wang, Z.-W. Liu and J. Lu, *Appl. Catal. A: Gen.*, 2008, **344**, 114-123.
54.   M. Oubenali, G. Vanucci, B. Machado, M. Kacimi, M. Ziyad, J. Faria, A. Raspolli-Galetti and P. Serp, *ChemSusChem*, 2011, **4**, 950-956.
55.   H. Li, L. Han, J. Cooper-White and I. Kim, *Green Chem.*, 2012, **14**, 586-591.
56.   Z. Sun, Y. Zhao, Y. Xie, R. Tao, H. Zhang, C. Huang and Z. Liu, *Green Chem.*, 2010, **12**, 1007-1011.
57.   X. Yang, X. Wang and J. Qiu, *Appl. Catal. A: Gen.*, 2010, **382**, 131-137.
58.   X. Tan, W. Deng, M. Liu, Q. Zhang and Y. Wang, *Chem. Commun.*, 2009, 7179-7181.
59.   A. E. Shanahan, J. A. Sullivan, M. McNamara and H. J. Byrne, *New Carbon Mater.*, 2011, **26**, 347-355.
60.   L. Xing, F. Du, J.-J. Liang, Y.-S. Chen and Q.-L. Zhou, *J. Mol. Catal. A: Chem.*, 2007, **276**, 191-196.
61.   H. B. Pan, C. H. Yen, B. Yoon, M. Sato and C. M. Wai, *Synth. Commun.*, 2006, **36**, 3473-3478.
62.   X. R. Ye, Y. Lin and C. M. Wai, *Chem. Commun.*, 2003, 642-643.
63.   A. Corma, H. Garcia and A. Leyva, *J. Mol. Catal. A: Chem.*, 2005, **230**, 97-105.
64.   N. Karousis, G.-E. Tsotsou, N. Ragoussis and N. Tagmatarchis, *Diam. Rel. Mater.*, 2008, **17**, 1582-1585.
65.   J.-H. Olivier, F. Camerel, R. Ziessel, P. Retailleau, J. Amadou and C. Pham-Huu, *New J. Chem.*, 2008, **32**, 920-924.
66.   S. Santra, P. Ranjan, P. Bera, P. Ghosh and S. K. Mandal, *RSC Adv.*, 2012, **2**, 7523-7533.

67.   A. Kongkanand, S. Kuwabata, G. Girishkumar and P. Kamat, *Langmuir*, 2006, **22**, 2392-2396.
68.   T. S. Miller, S. Sansuk, S. P. E, S. C. S. Lai, J. V. Macpherson and P. R. Unwin, *Catal. Today*, 2015, **244**, 136-145.
69.   B. Wu, D. Hu, Y. Yu, Y. Kuang, X. Zhang and J. Chen, *Chem. Commun.*, 2010, **46**, 7954-7956.
70.   W. Yang, X. Liu, X. Yue, J. Jia and S. Guo, *J. Am. Chem. Soc.*, 2015, **137**, 1436-1439.
71.   Y. Zhao, L. Fan, J. Ren and B. Hong, *Int. J. Hydrogen Energy*, 2014, **39**, 4544-4557.
72.   B. Li, J. Wang, Y. Yuan, H. Ariga, S. Takakusagi and K. Asakura, *ACS Catal.*, 2011, **1**, 1521-1528.
73.   W.-D. Zhang, B. Xu and L.-C. Jiang, *J. Mater. Chem.*, 2010, **20**, 6383-6391.
74.   W. Wang, P. Serp, P. Kalck and J. L. Faria, *J. Mol. Catal. A: Chem.*, 2005, **235**, 194-199.
75.   L.-C. Chen, Y.-C. Ho, W.-S. Guo, C.-M. Huang and T.-C. Pan, *Electrochim. Acta*, 2009, **54**, 3884-3891.
76.   B. Gao, G. Z. Chen and G. Li Puma, *Appl. Catal. B*, 2009, **89**, 503-509.
77.   B. Liu and H. C. Zeng, *Chem. Mater.*, 2008, **20**, 2711-2718.
78.   K. Byrappa, A. S. Dayananda, C. P. Sajan, B. Basavalingu, M. B. Shayan, K. Soga and M. Yoshimura, *J. Mater. Sci.*, 2008, **43**, 2348-2355.
79.   X.-H. Xia, Z.-J. Jia, Y. Yu, Y. Liang, Z. Wang and L.-L. Ma, *Carbon*, 2007, **45**, 717-721.
80.   M. M. Gui, S.-P. Chai, B.-Q. Xu and A. R. Mohamed, *RSC Adv.*, 2014, **4**, 24007-24013.
81.   L. Jiang and L. Gao, *Mater. Chem. Phys.*, 2005, **91**, 313-316.
82.   M. Ahmad, E. Ahmed, Z. L. Hong, W. Ahmed, A. Elhissi and N. R. Khalid, *Ultrason. Sonochem.*, 2014, **21**, 761-773.
83.   K. Gong, P. Yu, L. Su, S. Xiong and L. Mao, *J. Phys. Chem. C*, 2007, **111**, 1882-1887.
84.   Y. Liang, H. Wang, P. Diao, W. Chang, G. Hong, Y. Li, M. Gong, L. Xie, J. Zhou, J. Wang, T. Z. Regier, F. Wei and H. Dai, *J. Am. Chem. Soc.*, 2012, **134**, 15849-15857.
85.   N. I. Andersen, A. Serov and P. Atanassov, *Appl. Catal. B*, 2015, **163**, 623-627.
86.   Z. Liu, J. Wang, D. Xie and G. Chen, *Small*, 2008, **4**, 462-466.
87.   J. H. Park, J. M. Ko and O. Ok Park, *J. Electrochem. Soc.*, 2003, **150**, A864-A867.
88.   G. Arabale, D. Wagh, M. Kulkarni, I. S. Mulla, S. P. Vernekar, K. Vijayamohanan and A. M. Rao, *Chem. Phys. Lett.*, 2003, **376**, 207-213.
89.   C. Bittencourt, A. Felten, E. H. Espinosa, R. Ionescu, N. Moreau, P. Heszler, C. G. Granqvist, J. J. Pireaux and E. Llobet, *Smart Mater. Struct.*, 2006, **15**, 1555.
90.   C. Yujin, Z. Chunling and W. Taihong, *Nanotechnology*, 2006, **17**, 3012.
91.   J. Lu, A. Ma, S. Yang and K. M. Ng, *J. Nanosci. Nanotechnol.*, 2007, **7**, 1589-1595.
92.   B.-Y. Wei, M.-C. Hsu, P.-G. Su, H.-M. Lin, R.-J. Wu and H.-J. Lai, *Sens. Actuators B*, 2004, **101**, 81-89.
93.   Y. X. Liang, Y. J. Chen and T. H. Wang, *Appl. Phys. Lett.*, 2004, **85**, 666-668.
94.   H. Yu, K. Zeng, X. Fu, Y. Zhang, F. Peng, H. Wang and J. Yang, *J. Phys. Chem. C*, 2008, **112**, 11875-11880.
95.   F. Peng, X.-b. Fu, H. Yu and H.-j. Wang, *New Carbon Mater.*, 2007, **22**, 213-217.
96.   K. Dai, T. Peng, D. Ke and B. Wei, *Nanotechnology*, 2009, **20**, 125603.
97.   R.-J. Wu, Y.-D. Ju and C.-C. Jeng, *J. Nanosci. Nanotechnol.*, 2010, **10**, 4213-4220.
98.   Y. Haldorai, A. Rengaraj, J.-B. Lee, Y. S. Huh and Y.-K. Han, *Synt. Met.*, 2015, **199**, 345-352.
99.   Y. Ou, J. Lin, S. Fang and D. Liao, *Chem. Phys. Lett.*, 2006, **429**, 199-203.
100.   Y. Li, J. Ding, J. Chen, C. Xu, B. Wei, J. Liang and D. Wu, *Mater. Res. Bull.*, 2002, **37**, 313-318.
101.   H. T. Tan, Y. Chen, C. Zhou, X. Jia, J. Zhu, J. Chen, X. Rui, Q. Yan and Y. Yang, *Appl. Catal. B*, 2012, **119–120**, 166-174.
102.   M. Cargnello, M. Grzelczak, B. Rodríguez-González, Z. Syrgiannis, K. Bakhmutsky, V. La Parola, L. M. Liz-Marzán, R. J. Gorte, M. Prato and P. Fornasiero, *J. Am. Chem. Soc.*, 2012, **134**, 11760-11766.
103.   A. Beltram, M. Melchionna, T. Montini, L. Nasi, R. J. Gorte, M. Prato and P. Fornasiero, *Catal. Today*, 2015, DOI: http://dx.doi.org/10.1016/j.cattod.2015.03.032.
104.   M. Gong, W. Zhou, M.-C. Tsai, J. Zhou, M. Guan, M.-C. Lin, B. Zhang, Y. Hu, D.-Y. Wang, J. Yang, S. J. Pennycook, B.-J. Hwang and H. Dai, *Nat. Commun.*, 2014, **5**, 4695.
105.   S. C. Tsang, Y. K. Chen, P. J. F. Harris and M. L. H. Green, *Nature*, 1994, **372**, 159-162.
106.   X. Pan and X. Bao, *Acc. Chem. Res.*, 2011, **44**, 553-562.
107.   Z. Chen, Z. Guan, M. Li, Q. Yang and C. Li, *Angew. Chem. Int. Ed.*, 2011, **50**, 4913-4917.
108.   S. Guo, X. Pan, H. Gao, Z. Yang, J. Zhao and X. Bao, *Chem. Eur. J.*, 2010, **16**, 5379-5384.
109.   Y. Long, J. C. Palmer, B. Coasne, M. Sliwinska-Bartkowiak and K. E. Gubbins, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17163-17170.
110.   R. M. M. Abbaslou, A. Tavassoli, J. Soltan and A. K. Dalai, *Appl. Catal. A: Gen.*, 2009, **367**, 47-52.
111.   X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo and X. Bao, *Nat. Mater.*, 2007, **6**, 507-511.

112. W. Zheng, J. Zhang, B. Zhu, R. Blume, Y. Zhang, K. Schlichte, R. Schlögl, F. Schüth and D. S. Su, *ChemSusChem*, 2010, **3**, 226-230.
113. H. Liu, L. Zhang, N. Wang and D. S. Su, *Angew. Chem. Int. Ed.*, 2014, **53**, 12634-12638.
114. J. Zhang, J.-O. Müller, W. Zheng, D. Wang, D. Su and R. Schlögl, *Nano Lett.*, 2008, **8**, 2738-2743.
115. D. Deng, L. Yu, X. Chen, G. Wang, L. Jin, X. Pan, J. Deng, G. Sun and X. Bao, *Angew. Chem. Int. Ed.*, 2013, **52**, 371-375.
116. M. V. Bracamonte, M. Melchionna, A. Stopin, A. Giuliani, C. Tavagnacco, Y. Garcia, P. Fornasiero, D. Bonifazi and M. Prato, *Chem. Eur. J.*, 2015.
117. E. Dujardin, T. W. Ebbesen, H. Hiura and K. Tanigaki, *Science*, 1994, **265**, 1850-1852.
118. P. M. Ajayan and S. Iijima, *Nature*, 1993, **361**, 333-334.
119. R. Marega, F. De Leo, F. Pineux, J. Sgrignani, A. Magistrato, A. D. Naik, Y. Garcia, L. Flamant, C. Michiels and D. Bonifazi, *Adv. Funct. Mater.*, 2013, **23**, 3173-3184.
120. P. M. Ajayan, O. Stephan, P. Redlich and C. Colliex, *Nature*, 1995, **375**, 564-567.
121. B. C. Satishkumar, A. Govindaraj, M. Nath and C. N. R. Rao, *J. Mater. Chem.*, 2000, **10**, 2115-2119.
122. D. Zhang, C. Pan, L. Shi, L. Huang, J. Fang and H. Fu, *Microporous and Mesoporous Materials*, 2009, **117**, 193-200.

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