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Synergic Effect on Oxygen Reduction Reaction of Strapped Iron Porphyrins Polymerized around Carbon Nanotubes

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In the context of the development of new bio-inspired catalysts, MN4 complexes exhibit a great potential for small molecules activation in. In particular, metallated porphyrins and phthalocyanines combined with carbon nanotubes have been tested for the oxygen reduction reaction electrocatalytic systems and these nanotube/MN4 hybrids demonstrated promising properties. Here, a series of hybrid materials made of multi-walled carbon nanotubes (MWNTs) coated with strapped porphyrins have been fabricated. Iron porphyrin derivatives have been polymerized around the nanotubes via Hay-coupling and the resulting materials have been fully characterized. Two porphyrins have been probed; both are strapped with the same skeleton and differ only by the presence or not of overhanging carboxylic acids. In the porphyrin, the carboxylic acid group can possibly act as a proton relay between the medium and the catalyst. Whereas the presence of the carboxylic acid groups (acting as intramolecular proton relays) does not exhibit a significant influence on the catalytic properties, the combination of both components - MWNTs and porphyrin - leads to a better catalytic activity than those of the nanotubes or the porphyrins taken separately. The synergic affect is due to MWNTs which ensure the availability of electrons to the porphyrin catalysts and allow the ORR to occur via the 4-electron pathway, avoiding the production of hydrogen peroxide.

Introduction

For the last decade, the development of non-noble metal or metal-free catalysts for hydrogen economy has been a field of growing interest. Among others, Hydrogen Evolution Reaction (HER), 1 5 Hydrogen Oxidation Reaction (HOR), 6 8 Oxygen Evolution Reaction 9 11 and Oxygen Reduction Reaction (ORR) 12 16 are crucial reactions that must be well controlled to improve the production of hydrogen or to develop fuel cells based on non-noble metal catalysts. The reduction of oxygen is the reaction processing at the cathode of a fuel cell. Its slow kinetics, its multistep process and the competition between the 2-electron and 4-electron pathway make ORR the limiting kinetics, its multistep process and the competition between the 2-electron and 4-electron pathway make ORR the limiting factor. 20 Initially demonstrated for tris(2-aminoethyl)amine (tren)-capped porphyrins lacking a second metal cation in the "tren" coordination site; this a priori surprising result was later extended to picket and non-functionalized strapped porphyrins and culminated with the hangman catalyst family in which a carboxylic acid group acting as proton relay is associated to the metallic center. 27 29 This concept was further applied to the study of meso-tetraarylporphyrins bearing four carboxylic acid groups either in ortho or para position of the meso aromatic cycles. It has been shown that in the case of the ortho substitution, the selectivity was high for the 4e- process avoiding the production of hydrogen peroxide. 30 Finally, it is now well admitted that porphyrin, corrole and phthalocyanine derivatives constitute prolific materials for electrocatalysis. 23 Within the context of the replacement of platinum in fuel cells, we and others envisioned the use of porphyrin or phthalocyanine-functionalized carbon nanotubes in

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Electronic Supplementary Information (ESI) available: Experimental details, additional images, spectra and electrochemical data. See DOI: 10.1039/x0xx00000x
In such systems, the macrocycle catalytic sites are supported on carbon nanotubes acting as conducting materials. Generally, the macrocycles are just adsorbed on the nanotube surface but recently we reported a new method of functionalization based on the templated polymerization of meso-tetraethylporphyrin around the nanotubes. This method was also used by other groups and extended to the synthesis of iron-phthalocyanine via tetramerization of 1,2,4,5-benzenetetranitrile in the presence of FeCl₃ around MWNT. Herein, we tested the ORR activity of MWNTs functionalized with iron (III) strapped porphyrins. MWNT-FeP(9) and MWNT-FeP(10) are synthesized by polymerization of the proper strapped porphyrins containing propargyloxy groups around the nanotubes by Hay-coupling.

The porphyrins contain a bridge bearing two overhung carboxylic acid or ester functions between the phenyl groups in 5 and 15 meso positions (Scheme 1). The bridge prevents the aggregation of the porphyrins compared to the previous studies and we assume that only one face is available to interact with the nanotubes by π-stacking. The goal of this study is first to measure the ORR properties of strapped porphyrins bearing a proton relay and second to evaluate the influence of the communication between the nanotube and the catalytic centers as well as the effects of the non-aggregation of the porphyrins.

Results and discussion

Synthesis

The general synthetic pathway for porphyrin derivatives is presented in Scheme 1. The reaction sequence started with the synthesis of the propargyloxy-functionalized aromatic aldehyde 1 and 2. The reaction of 2 with an excess of pyrrole led to the 2-nitroaryldipyrromethane 3 which, condensed on aldehyde 1, was converted into porphyrin 4 whose nitro functions were reduced by the usual methods to obtain porphyrin 5. Reaction of the purified atropisomer αα of 5 with 3-chloromethyl benzoic chloride furnished bis-picket porphyrin 6 which was treated in alkaline conditions with either diethyl malonate or di-tert-butyl malonate to give rise to the strapped ligands 7a-b. The ester groups of porphyrin 7a (R₁ = tBu) were cleaved by treatment with HCl (1 M) at room temperature for 48h leaving the propargyloxy groups unaffected and leading to porphyrin 8. Finally porphyrins 8 and 7b (R₁ = Et) were metallated with iron (II) bromide in THF to give 9 and 10, respectively (see ESI for experimental details and characterization).

The X-ray structure of porphyrin 9 was solved (Fig. 1) and it established that one of the two carboxylic acid groups is coordinated to the ferric cation as its fifth ligand with a bond length for O1-Fe of 1.945 Å. The iron(III) cation is bound 0.512 Å out of the mean porphyrin plane (24MP) towards its fifth ligand. However, with this strap linked on two opposite meso positions (5, 15), it has been shown on a bis-strapped analogous complex that the coordination of the overhanging carboxylic acid on the iron(III) cation was not possible. The porphyrin is saddle-shaped together with a significant ruffling as indicated by an average angle between the two pairs of opposed pyrroles of 20.24°. The W-shaped strap, disordered over two positions is almost perpendicular to the porphyrin plane (angle between the two mean planes of 84.28°).

![Fig. 1 Oak Ridge thermal ellipsoid plot (ORTEP, 30% thermal ellipsoids) representation (left) and apical rod view (right) of the X-ray structure of iron (III) porphyrin 9.](image)

The synthesis of the hybrid MWNT/strapped porphyrin materials MWNT-FeP(9) and MWNT-FeP(10) is presented in Fig. 2. Purified MWNTs were dispersed in N-methylpyrrolidone (NMP), then 9 or 10 were added and the mixture was gently sonicated and then let sit for 30 min. Then
a freshly prepared mixture of copper(I) chloride and \(N,N',N',N'-\)tetramethylethlenediamine (TMEDA) was added and the reaction was stirred at room temperature for 24h under an atmosphere of oxygen. After reaction, the nanotube materials were purified by filtration through 0.2µm PTFE membrane and washed with NMP (to remove unreacted porphyrins), water, \(\text{NH}_4\text{Cl}\) solution (to remove the copper catalyst) and then again with water and NMP (see ESI).

The nanotube hybrids were characterized by absorption, Raman and X-ray photoemission (XPS) spectroscopy while their morphologies were investigated by electronic microscopies (SEM and TEM). Finally, their ORR activity was studied using Rotating Ring-Disk Electrode (RRDE) at different pH.

First XPS gives us qualitative information on the elemental composition of our hybrid materials. The XPS spectra of MWNT, MWNT-FeP(9) and MWNT-FeP(10) are presented in Fig. 3a; the peaks labelled (*) on the spectra are due to fluorine (\(F_{1s}\)) arising from the PTFE supporting membrane and the peaks labelled (**) are due to oxygen Auger lines (O\(_{KLL}\)). For MWNT, the spectrum shows only the presence of carbon and a bit of oxygen (coming from the oxidative purification treatment) whereas the spectra of MWNT-FeP(9) and MWNT-FeP(10) show the presence of nitrogen and iron coming from the porphyrins. The high resolution spectra of the carbon (right part of Fig. 3a) for MWNT show mainly the contribution of \(sp^2\) carbon atoms of the nanotubes; the C1s spectrum of MWNT-FeP(9) exhibit a very different pattern with contributions at higher binding energy due to the presence of the organic materials (i.e., the porphyrins) around the nanotubes. XPS also permits to estimate the atomic concentration of iron: it is around 0.1 and 0.08 atomic % for MWNT-FeP(9) and MWNT-FeP(10), respectively. Note that these values are not representative because of the margin of error on the analysis; nevertheless they show that these materials contain iron. The absorption spectrum (Fig. 3b) of MWNT shows a strong absorption in the UV region and a monotonic decrease of the absorption signal in the visible and NIR region. Conversely, the spectra of MWNT-Fe(9) and MWNT-Fe(10) exhibit signals at ca. 425 nm with shoulder in the 500-600 nm region arising from the Soret and the Q-bands of the porphyrins.

Fig. 3 a) XPS spectra of MWNT (black), MWNT-FeP(10) (blue) and MWNT-FeP(9) (red); on the right deconvoluted XPS core level spectra of carbon C\(_{1s}\) of MWNT and MWNT-FeP(9) and iron Fe\(_{2p3/2}\) of MWNT-FeP(9). The signals labelled (*) and (**) are due to fluorine from the PTFE membrane and the oxygen Auger lines, respectively; b) UV-Vis-NIR absorption spectra of MWNT (black), MWNT-FeP(10) (blue) and MWNT-FeP(9) (red); c) Raman spectra recorded with excitation at 532 nm of MWNT (black), MWNT-FeP(9) (red) and porphyrin 9 (green).

The Raman spectra of MWNT, MWNT-FeP(9) and Fe-porphyrin 9 taken as reference are shown in Fig. 3c. The spectrum of MWNT shows the typical first order graphical mode (G band) at 1570 cm\(^{-1}\) and defect band (D band) at 1330 cm\(^{-1}\) as well as the second order 2D and D+G in the 2500-3000 cm\(^{-1}\) region. The iron porphyrin (green spectrum) exhibits several bands at 350 cm\(^{-1}\) and between 1000 and 1600 cm\(^{-1}\); these bands can be clearly identified in the spectrum of MWNT-FeP(9), in addition to the D, G, 2D and D+G bands, confirming the presence of the porphyrin on the nanotubes. Interestingly, we were not able to observe the characteristic bands of the triple bond at around

![Fig. 2 Schematic representation of the synthesis of MWNT-FeP(9) and MWNT-FeP(10): i) CuCl, TMEDA, NMP, O\(_2\), RT.](image-url)
2100 cm\(^{-1}\) neither in the porphyrin nor in the functionalized nanotubes, even when Raman spectroscopy was performed with excitation at 476 nm (Fig. S1). By Infrared spectroscopy, very weak bands at 2115 cm\(^{-1}\) corresponding to the stretching band of the C≡C bonds were observed for FeP(9) and FeP(10) (Fig. S2); unfortunately, this band could not be observed in the nanotube hybrids certainly because they strongly absorb IR making the observation of weak peaks difficult.

The nanotube/porphyrin hybrids were studied by scanning and transmission electron microscopy (SEM and TEM). SEM images are presented in Fig. 4a. In the physisorbed hybrid MWNT-FeP(11) (left part), the images show that the porphyrins tend to segregate and form bubbles of organic materials at the extremity of the nanotubes and dried drops on the silicon surface. This observation supports the fact that the interactions between the porphyrins and the nanotubes are quite weak and the two components can segregate in the catalytic inks. On the contrary, for the polymerized hybrid MWNT-FeP(9), the nanotube surfaces appear homogeneous with no aggregates detected (Fig. 4a, right part). So we believe that the porphyrin are exclusively located and homogeneously distributed on the nanotube surfaces. Unfortunately, the limited resolution of SEM does not permit to observe porphyrin coating. This was achieved owing to TEM analysis: the images of MWNT-FeP(9) (Fig. 4a and S3) show the presence of a thin layer of organic materials on the nanotubes. For comparison, TEM images of MWNT (Fig. S3) do not show the presence of organic material on the nanotube surfaces.

### Oxygen reduction reaction activity

We now turn to the characterization of the ORR activity of the nanotube/porphyrin hybrids. As a reference material for ORR, we also prepared MWNT-FeP(11) in which iron (iii) porphyrin 11 is simply adsorbed on the nanotube sidewalls (see structure in ESI). Fig. 5 presents the electrocatalytic properties for the reduction of oxygen of the different components: MWNT, Fe-porphyrin 9, MWNT-FeP(9), MWNT-FeP(10) and MWNT-FeP(11) at pH 10, 8 and 6 deposited on the Glassy Carbon (GC) electrode recorded at 800 rpm; the complete cycles (from 0 to 2000 rpm) for all hybrids are given in Fig. S4-S6. All the curves correspond to the average (reduction and reoxidation) of the cyclic voltammetry curves. First of all, the RDE curves (Fig. 5a-c) show that the catalytic inks made by mixing the nanotubes with the porphyrins exhibit higher current density and lower overpotential (of about 0.1 to 0.25V depending on the pH) than porphyrins alone. The current density is related to the number of electrons involved in the reduction of oxygen. Thus, the increase of current density suggests that the nanotube/porphyrin catalytic inks permit to reduce oxygen via a process involving a higher number of electrons than catalytic the inks made only with iron porphyrins. The presence of the nanotubes is therefore extremely important to improve the ORR properties. We believe that it is due to the conductivity of the nanotubes which facilitates the access of the electrons to the catalytic centers. This result is not surprising since Rigby et al., demonstrated that the mesoscale environment around the catalyst (iron porphyrins) plays a crucial role on the resulting properties. It is also worth mentioning that MWNT (black curve) reduced oxygen with a lower overpotential and a higher current density than FeP 9. However, compared to the three MWNT/FeP hybrids, MWNT alone exhibit current densities of ca. 1 mA/cm\(^2\) lower (at −0.6V vs Ag/AgCl) than those of the hybrids. Indeed, it was found that at low potential carbon nanotubes reduce oxygen via a 2-electron process to give hydrogen peroxide. Fig. 5a-c also shows the comparison between the ORR activity of MWNT-FeP(11) (the reference in which Fe-porphyrin 11 is simply adsorbed on the nanotubes), MWNT-FeP(10) (the polymerized nanotube-porphyrin hybrid in which the proton relay is absent) and MWNT-FeP(9) (the polymerized nanotube-porphyrin hybrid containing proton relays). At all the considered pH, the polymerized hybrids MWNT-FeP(9) show slightly better properties than the hybrids in which the porphyrins are simply mixed with the nanotubes (MWNT-FeP(11)). A possible explanation of this observation comes from SEM images. Indeed, one can see that in MWNT-FeP(11) (Fig. 5a – left part), the porphyrin tends to segregate and form drop-shaped aggregates on the nanotubes. Conversely, in the polymerized hybrids, the porphyrin seems better dispersed along the nanotubes. This result suggests that the catalytic activity of the porphyrins is better when there are in close contact with the nanotube surfaces. In the case of the polymerized hybrids, the comparison between MWNT-FeP(9) and MWNT-FeP(10) does not permit to conclude that the presence of proton relays has a significant influence on the
ORR activity of the strapped porphyrins. Indeed even at pH 6, the curves are very similar and only a slight difference of 20-30 mV of the reduction potential is observed. The close proximity of the proton donor group to the iron center does not seem to be a prerequisite to influence significantly the electrocatalytic properties. The presence of Nafion in the mixture likely ensures the availability of proton close to the reaction center.

![Graphs showing ORR activity](image)

**Fig. 5** RDE curves (rotation rate of 800 rpm) recorded for ORR in O₂-saturated phosphate buffer solutions at pH 10 (a), pH 8 (b) and pH 6 (c) (scan rate = 5 mV s⁻¹, room temperature) on GC with predeposited FeP (9) (green), MWNT (black), MWNT-FeP(11) (orange), MWNT-FeP(10) (blue) and MWNT-FeP(9) (red). d) RDE measurements of oxygen reduction (negative current) and hydrogen peroxide oxidation (positive current) for MWNT (black), FeP (9) (green), and MWNT-FeP(9) (red) at pH 10, pH 8 and pH 6 (from left to right) in O₂-saturated phosphate buffer solutions. The ring electrode was polarized at 0.8 V vs Ag/AgCl. Rotation rate: 400 rpm; scan rate: 5 mV s⁻¹.

Fig. 5d shows the RRDE curves registered at a rotation rate of 400 rpm for MWNT, FeP (9) and MWNT-FeP(9) at various pH. The number of electrons involved in the reduction of oxygen for MWNT-FeP(9) and for the porphyrin FeP (9) and the MWNT used as references was determined using the current detected at the ring electrode using Eq. 1.⁴⁷

\[
N = \frac{4I_{\text{disk}}}{I_{\text{ring}}} (\text{Eq. 1})
\]

\(N_C\), the collection coefficient (0.2) was determined using the one-electron Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ redox couple and \(I_{\text{disk}}\) and \(I_{\text{ring}}\) were determined on the RRDE curves. The numbers of electrons involved in the reduction as well as the onset potentials for the reduction are collected in Table 1. From the ring current curves of Fig. 5d, one can observe directly that the reduction of O₂ is accompanied by the production of hydrogen peroxide both for MWNT and FeP (9). Conversely, for MWNT-FeP(9), almost no production of H₂O₂ is detected.

**Table 1.** Onset potential for the reduction of oxygen and number of electrons involved in the reduction at -0.6V vs Ag/AgCl.

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<tr>
<td>FeP (9)</td>
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<td>3.29</td>
<td>-0.25</td>
<td>3.32</td>
<td>0.04</td>
<td>3.69</td>
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<tr>
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<td>-0.13</td>
<td>3.90</td>
<td>0.03</td>
<td>3.85</td>
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<tr>
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<td>3.96</td>
<td>-0.04</td>
<td>3.95</td>
<td>0.10</td>
<td>3.97</td>
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The onset potential for ORR of the hybrid materials is found to be -0.07, -0.04 and 0.10 V vs Ag/AgCl from pH 10 to pH 6 that means 0.13, 0.16 and 0.30V vs NHE since the potential of Ag/AgCl reference vs NHE is 0.198V. The thermodynamic potentials for the reduction for the reduction of oxygen are ca. 0.63V at pH 10, 0.75V at pH 8 and 0.87V at pH 6. This result shows that our hybrid materials present a quite large overpotential of ca. 0.5-0.6V compared to the thermodynamic potential for the reduction of oxygen.

**Conclusions**

We described the synthesis of new strapped iron(III)-porphyrin and the subsequent formation of hybrid materials with carbon nanotubes for oxygen reduction reaction purposes. The electrocatalytic activity of porphyrins bearing carboxylic groups expected to act as proton relay during the reduction of O₂ was studied and compared with their direct precursor containing ethyl ester groups. First, the hybrid nanotube/porphyrin materials exhibit much better ORR activity than the two components (nanotubes and Fe(III)-porphyrins) alone as the nanotube/porphyrin hybrids reduce oxygen in water via a 4-e⁻. Second, no significant improvement of the ORR activity due to the presence of proton relay in the hybrids (especially at pH 6) was observed. The presence of Nafion in the catalytic inks ensures a sufficient supply of protons during the reaction. This second observation underlines the essential need of control reactions with reference catalysts to probe the actual influence of additional groups on the activity of such catalysts. Finally, it is worth mentioning that the results obtained here are difficult to compare to literature since the conditions used to characterize the properties are never the same from one report to another. Furthermore, it was suggested that the environment of the catalyst at the mesoscale play a crucial role on the performances.⁴⁵ The hybrids presented here exhibit overpotential for the reduction of oxygen of ca. 0.5-0.6V compared to the thermodynamic potential.

**Conflicts of interest**

There are no conflicts to declare.

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Notes and references