

Letters to the Editor

Adsorption of carbon nanotubes on active carbon microparticles

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Functionalised carbon nanotubes (f-CNTs) are exploited for a wide range of applications both in materials science and biomedicine [1–6]. It has been recently demonstrated that f-CNTs can be adsorbed or covalently linked to silica-based microspheres aiming to the development of new efficient stationary phases for high pressure liquid chromatography separations [7]. Another class of particles with micrometer dimensions comprises the high porosity activated carbon microspheres, which can be used in the purification of plasma and blood from toxic molecules and metabolites [8,9]. Granular and fibrous activated carbons have been developed as adsorbents for efficient elimination of bilirubin from protein solutions [10]. Within this family of carbon-based materials, haemosorbent granulated deliganding (HSGD) activated carbon is a novel form of active carbon [11,12]. HSGD appears as black spheres with a diameter comprised between 200 and

300 μ m, a bulk density γ equal to 0.12–0.20 g/cm³ and a total benzene pore volume V_s of 2.06–2.5 cm³/g. HSGD is currently used for adsorptive treatment in liver failure [13] and proposed for the removal of uremic protein-bound toxins [14]. Alternatively, the covering of these spheres with native DNA or dextran sulfate enhances its affinity to anti-DNA-antibodies and proinflammatory cytokines [15].

The aim of this study is to explore the capacity of the HSGD surface to adsorb *f*-CNTs, similarly to DNA and dextran sulfate. This is the first step towards the generation of new combined adsorbents, using functionalised nanotubes as specific ligands, and/or the preparation of new adsorbents by modifying the distribution and the accessibility to the pores of precursor activated carbon. HSGD has been prepared through a pyrolysis process of nitrogen-containing synthetic resins (vinylpyridine-styrene-divinylbenzene copolymer)

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Fig. 1 – Functionalisation of MWNTs by strong acid treatment.

(See Supporting Information for more details on the physicochemical characterization of HSGD). The resulting microparticles contain aromatic groups and small amounts of carboxyl, carbonyl and hydroxyl groups generated during the carbonization and activation process (See also Small-Angle Neutron Scattering (SANS) and FT-IR characterization of HSGD displayed on Figure S1 and S4 of the Supporting Information). The percentage of the nitrogen is lower than 1%. To create the new HSGD adsorbent modified with carbon nanotubes, we have used the oxidised nanotubes. Both single-walled (SWNTs) and multi-walled carbon nanotubes (MWNTs) have been shortened using strong acid conditions to generate a high amount of carboxylic groups at the tips and around the side walls (Fig. 1) (see Supplementary Information for the experimental details) [16–18].

The oxidised CNTs formed highly stable suspensions in pure water at 1 mg/ml. No precipitation was observed after storing at 4 °C for several months. Both oxidised SWNTs and MWNTs were mixed with HSGD beads to verify the capacity of the latter to adsorb the tubes. Different types of conditions were tested. The nanotubes at 1 mg/ml in water were diluted in acid or basic solutions, and in solutions containing different types of salts, and subsequently added to the HSGD microparticles (Table 1 and Tables S2 and S3). In a typical experiment, 0.5 ml of HSGD (corresponding to 90 mg of microspheres, as calculated by the bulk density γ value of 0.18 g/cm³ and confirmed by direct weight) were gently shaken in a total volume of 2 ml of solution up to 90 h at room temperature. The change of the colour of the solution was monitored visually. We have assigned a code to the different colours at the end of the incubation time: three dots for black,

two dots for grey, and one dot for pale grey/transparent. A correlation between the colours of the solutions and the amount of nanotubes adsorbed onto HSGD at the end of the incubation time was established using UV-vis spectroscopy. In the case of samples identified as black less than 25% of f-CNT were adsorbed at the end of the process (i.e. Entry 4, Table 1). For the grey samples (i.e. Entry 1, Table 1) we have calculated an adsorption between 30% and 50% of nanotubes, while in the case of the efficient adsorption (i.e. Entry 2, Table 1) more than 80-85% of nanotubes were bound to the HSGD phase at the end of the incubation time. For comparison we have also studies oxidised SWNTs. Surprisingly, the behaviour of these nanotubes was completely different. SWNT-COOH immediately precipitated when added to 0.9% of NaCl or KCl (Table S3 and Fig. S8). Indeed, these tubes tend to rebundle because of the salt effect as it has been recently described for single-walled carbon nanotubes suspended in sodium dodecyl sulphate [19]. Reaggregation of oxidised SWNTs occurred also when the tubes were added to HSGD simply in water although after few hours. The presence of SWNTs flocks on the HSGD spheres was clearly visible. The adsorption of SWNTs on HSGD was therefore ineffective and not further investigated. On the contrary, oxidised MWNTs were very efficiently adsorbed on HSGD. After eliminating the solvent and drying the particles at 60–70 °C, the release of tubes was negligible when the particles redispersed in H₂O. (Entry 1–3, 5, 6 and 9, Table 1). In particular, we found that HSGD reached saturation in the adsorption capacity, since by increasing the amount of nanotubes the microparticles were unable to totally adsorb them from the solution (Entry 4, 7, 8 and 10, Table 1).

Another interesting feature we observed was the effect of the counter ions. Using solutions of sodium chloride or potassium chloride, the solution of nanotubes in contact with the HSGD beads became transparent in few hours (Entry 2 and 3, Table 1). After the addition of the nanotubes, dispersed in the solution of NaCl or KCl, to the HSGD spheres we measured an increase of pH from neutral (nanotubes alone) to basic (nanotubes mixed with HSGD). This is probably due to a nucleophilic or radical reaction of chloride at the active surface of HSGD which renders basic the pH by releasing hydro-

Table 1 – Parameters and different types of conditions tested for the adsorption of f-CNTs on HSGD microparticles					
Entry	<i>f</i> -CNT (ml)	Solution (ml)	Incubation time (h)	pН	Solution colour
1 ^a	0.125	Pure water (1.875)	10	7	••
2 ^a	0.125	0.9% NaCl (1.875)	4	10	•
3 ^a	0.125	0.9% KCl (1.875)	4	10	•
4 ^a	0.25	Pure water (1.75)	90	10	•••
5 ^a	0.25	0.9% NaCl (1.75)	10 (24)	10	●● (●)
6 ^a	0.25	0.9% KCl(1.75)	10 (24)	10	●● (●)
7 ^a	0.5	0.9% NaCl (1.5)	72	10	•••
8 ^a	0.5	0.9% KCl (1.5)	72	10	•••
9 ^b	0.125	10 mM HCl (1.875)	0.5	2	•
10 ^b	0.5	10 mM HCl (1.5)	48	2	•••

The amount of HSGD is 0.5 ml (90 mg). The total volume of the final solution is 2 ml. MWNT-COOH are solubilised in pure water at 1 mg/ml. The solution of 1 mg/ml of *f*-CNTs (column 2 of the Table) is diluted in water and in the different saline or acid solutions, to a total volume of 2 ml (corresponding to the sum of the volumes of the columns 2 and 3 of the Table), and it is added to the HSGD particles. Following this addition the pH was measured immediately. (●●) Black; (●) Grey; (●) Pale grey or transparent.

a HSGD is washed with pure water before the addition of MWNT-COOH solution.

b HSGD is not washed before the addition of MWNT-COOH solution.



Fig. 2 – Kinetics of the adsorption of oxidised MWNTs solubilised in 0.9% NaCl (Entry 2, Table 1) onto HSGD microparticles.

xyl groups. The adsorption was extremely rapid in 10 mM HCl, thus confirming that the chloride plays an important role in the adsorption capacity (Entry 9, Table 1).

We have measured the kinetics of adsorption onto HSGD of the oxidised CNTs solubilised in 0.9% NaCl (Entry 2, Table 1). The decrease of the UV–vis adsorption band at 600 nm of MWNT-COOH was measured at different time points (Fig. 2). At the end of the process more than 90% of nanotubes were adsorbed onto HSGD as already reported in Table 1. The MWNT-COOH followed a second order exponential pseudomonomolecular adsorption reaction (the concentration of HSGD is constant being in high excess). The interpolation of the data gave values of the two rate constants corresponding



Fig. 3 – TEM images of MWNT-COOH. Top: MWNT-COOH dispersed in water. Bottom: MWNT-COOH in 0.9% NaCl solution after contact with HSGD for 1 h (Entry 2, Table 1).

to $k_1 = (0.0323 \pm 0.0025) \text{ s}^{-1}$ and $k_2 = (0.0263 \pm 0.0033) \text{ s}^{-1}$, respectively.

This experiment was repeated twice obtaining comparable values for the two constants (Fig. S9). The adsorption of the nanotubes proceeded with two rate constants. This is probably due to the polydispersity of the nanotubes. Indeed, the nanotubes are within a range of lengths comprised between 50 and 500 nm. Most of the nanotubes are rapidly adsorbed while a small fraction seems to adsorb more slowly. It is also possible that part of tubes is aggregated in solution and part is composed of individualised tubes. This would give rise to the second order kinetics. We have checked the solution of the nanotubes after contact with the HSGD phase (Fig. 3 and Fig. S10). It seems that the content of the short CNTs becomes less after this contact, which means the short CNTs adsorb much easier on the surface of HSGD. In addition, during the incubation time, the salts likely induce a slight reaggregation of f-CNTs which do not remain well dispersed like in water.



Fig. 4 – SEM images of MWNT-COOH adsorbed on HSGD microparticles. Top images: These beads correspond to a sample derived from a preliminary experiment in which HSGD (0.5 ml) was mixed with 0.5 ml of MWNT-COOH in water for 3 hours following a slow evaporation of the solution at 80–90 °C. Middle images: diluted MWNT-COOH are mixed with HSGD in 0.9% NaCl solution (Entry 1, Table S2). Bottom images: concentrated MWNT-COOH are mixed with HSGD in 0.9% NaCl solution (Entry 3, Table S2). These two images are relative to different micropheres of the same sample taken at different magnifications.

After absorption, the solution where the HSGD particles and the nanotubes were dispersed was eliminated, and the modified HSGD phase was washed once with water. We have measured a release of CNTs of about 8%. This confirms how the procedure of drying the microparticles after complete adsorption of the nanotubes is necessary to definitely fix the tubes to the active charcoal (see above).

The different carbon nanotube modified HSGD beads were then analysed using scanning electron microscopy (SEM) (Fig. 4 and Fig. S11-S16). The SEM images of the HSGD microparticles which were not able to completely adsorb the oxidised MWNTs showed volcanic-like microcraters and oceanlike rifts composed of aggregated nanotubes all around the sphere (Fig. 4, top). Indeed, some of the samples with the highest amount of nanotubes, that were still black after 90 h, were subjected to a slow evaporation of the solvent at 80-90 °C to improve the adsorption of the tubes. However, this approach was not successful since part of the tubes was released after resuspension of the spheres in water and those adsorbed were clearly aggregated. The SEM images of the samples that were transparent after few hours displayed instead a homogenous carpet of tubes all around the surface (Fig. 4, middle and bottom). The nanotubes are clearly visible at the surface of the HSGD particles.

To inspect if MWNT-COOH were able to penetrate into the pores of HSGD microparticles, we have mechanically broken part of the spheres. The SEM images show that the nanotubes are not present inside the particles, but are adsorbed only at their surface (See Supporting Information, Fig. S17 and S18). It is probable that MWNT-COOH are too big thus hampering their penetration into the pores of HSGD. The type of interaction between MWNT-COOH and the surface of HSGD are of hydrophobic and π - π stacking nature since both materials are essentially hydrophobic and rich in aromatic moieties.

We have then performed some preliminary tests on the efficiency of the HSGD microparticles modified with the nanotubes to adsorb toxic metabolites. This new stationary phase was tested for its capacity to adsorb bilirubin diluted in albumin solution. Particularly, 50 mg of the HSGD-CNT microparticles, obtained by the incubation of the oxidised MWNTs in 0.9% NaCl or 10 mM HCl (Table 1, Entry 2 and 9), placed in contact with 6 ml of solution containing 292.4 mg/l of bilirubin and 26.57 g/l of albumin, were able to adsorb 7.34 mg of bilirubin and 0.23 mg of albumin per gram of HSGD-CNTs, respectively. The quantities of bilirubin and albumin were comparable to those adsorbed by HSGD without f-CNTs. These results demonstrate that the HSGD phase modified by the oxidised MWNTs maintains the same adsorptive power as HSGD alone. HSGD has the active adsorptive surface of about 2500-3000 m²/g and it can be improved to achieve a higher degree of modification that is probably necessary to adsorb a higher amount of nanotubes at the surface of microparticles.

In conclusion, we have described a novel combined adsorbent based on active charcoal modified with oxidised carbon nanotubes. The use of carbon nanotubes is based on the particular chemico-physical properties of this material. The tubular structure associated to the extended surface area of CNT might increase the total surface available for the specific interaction with biomolecules. In addition, the nanotubes with their highly hydrophobic surface character might modulate the adsorption of definite classes of ligands and serve as linker between HSGD surface and different bioactive ligands covalently bound to CNTs. As assessed by SEM the nanotubes are not able to penetrate into the pores. Therefore, the characteristics of the nanotubes can be exploited at the surface rather than inside the pores of HSGD. The properties of this new stationary phase as adsorbent for the interaction and eventual elimination of toxic molecules, metabolites and auto-antibodies are currently under study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.carbon.2008.03.010.

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Synthesis of C₆₀ nanoparticle doped hard carbon film by electrodeposition

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Hard carbon films have been used as protective coatings in various tribological and optical applications for their adjustable mechanical behavior and stability via the bond configuration [1]. However, high residual stress is generally present in these carbon films, which weakens the film/substrate bonding strength. The incorporation of metals or nonmetals [2–5] has been proved to be an efficient approach to reduce the residual stress of hard carbon films but with the sacrifice of hardness.

Carbon allotropes, such as fullerene and carbon nanotube, possess excellent mechanical properties, which inspires us to incorporate them into hard carbon films to reduce the internal stress and to retain or increase the hardness of hard carbon films simultaneously. Herein, we report a simple and effective method for the incorporation of C_{60} nanoparticles into hard carbon films fabricated by electrodeposition.

The deposited films were characterized by transmission electron microscopy (TEM), Raman spectroscopy, and Fourier transform infrared spectrometry (FTIR). Their mechanical properties were investigated on nanoindentation system. In

The experimental apparatus for the electrodeposition of hard carbon films has been described elsewhere [6]. A silicon wafer (100) with a size of $10 \times 20 \times 1 \text{ mm}^3$ was used as the substrate and negative electrode. A platinum plate served as the counter electrode. The distance between the substrate and the platinum plate was about 6 mm. Methanol was chosen as the electrolyte. The concentration of C₆₀ nanoparticles in the electrolyte was 0.28 mg mL⁻¹. All the films were deposited at an applied voltage of 1600 V and a constant temperature of 50 °C. The deposition time was 10 h and a gray-black film was finally obtained.

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