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Sorption properties of modified single-walled carbon nanotubes

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Abstract

Single walled carbon nanotubes (SWNTs), with high carboxylic acid content, were chemically modified in order to develop hydrophilic and organophilic analogues. The hydrophilic SWNTs were prepared by wrapping a water–soluble polymer, namely poly (sodium 4-styrene sulfonate) (PSSNa) around the pristine SWNTs, while the organophilic SWNTs were developed by forming amide bonds with oleylamine ($C_{18}H_{37}N$). The modification of carbon nanotubes was studied through IR spectroscopy. Moreover, the sorption properties of pristine and modified carbon nanotubes were studied by using adsorbates, which differ in polarity (i.e. water, ethanol and *n*-hexane). Based on these measurements it is concluded that the sorption behaviour of the SWNTs has been completely modified after the treatment, since the hydrophilic and organophilic carbon nanotubes reveal enhanced selectivity of water and *n*-hexane respectively.

Keywords: Carbon nanotubes; Sorption properties; Functionalization

1. Introduction

Carbon nanotubes (CNT) exhibit unique structural, mechanical, and electrical properties [1,2] and are intensely studied for possible use among else in polymer enhancement [3–5], nanoelectronics, as supporting material in catalysis [6–8], in nanodevices, nanobioelectronics etc. [9–11]. Moreover, CNTs due to their uniformity in size and surface properties are considered as ideal model sorbent systems for studying the effect of nano-pore size and surface properties on sorption and transport properties. In addition, the surface functionalization of CNTs by chemical methods offers to them the advantage to adapt in different applications [12–15]. In this way, it is possible to combine the unique properties of CNTs with that of other known materials such as polymers, metals, biomolecules, or organic molecules affording new materials with impressive properties and potential applications. For instance, the attachment of organic groups leads to CNT derivatives dispersible in organic solvents, compatible with polymers [16], whereas oxidized CNTs are favoured as supporting material for the deposition of metallic nanoparticles, which are used in catalysis [6–8]. Chemically modified CNTs can be used in drug delivery [17,18], as biosensors [19,20] and in many other applications. However, they have poor temperature stability and due to their macromolecular structure and their affinity to agglomeration are poorly soluble in solvents. The latter is an important roadblock that hampers their uniform incorporation into polymer matrices for the fabrication of advanced composite materials. This drawback can be alleviated through chemical modification or functionalization of carbon nanotube surfaces. Organically modified CNTs due to the controlled physical and chemical properties such as high surface area, hydrophilicity, hydrophobicity, permeability etc. could be used for the development of membranes for the selective gas separation [21,22].

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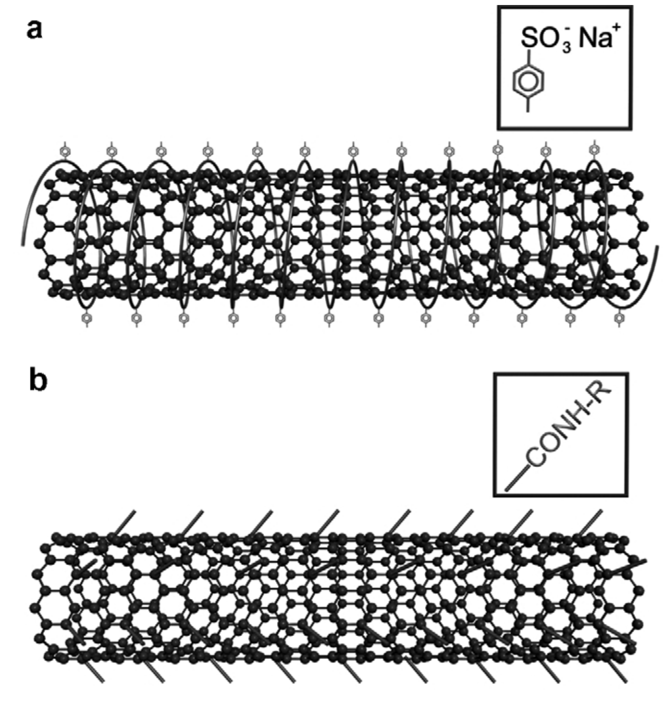

Fig. 1. (a) Hydrophilic SWNTs prepared by wrapping of the water–soluble poly (sodium 4-styrene sulfonate) around SWNTs and (b) organophilic SWNTs developed by forming amide bonds with oleylamine.

In this work, commercial SWNTs (purity 80–90%) with high carboxylic acid content were functionalized with oleylamine ($C_{18}H_{37}N$) and poly (sodium 4-styrene sulfonate) (PSSNa) separately in order to obtain hydrophobic and hydrophilic analogues respectively and to enhance the surface area by de-bundling (Fig. 1). The modified SWNTs were characterized by IR spectroscopy, while the sorption properties of both pristine and modified samples have been studied by using vapours of three different solvents, which differ in terms of their polarity (water, ethanol, and *n*-hexane) as sorbates.

2. Experimental

2.1. Description of pristine carbon nanotubes

The SWNTs used in this work were purchased from Carbon Solutions, Inc. According to the manufacturer, the distribution of outside diameters is centred around 1.4 nm and the length distribution is between 0.5 and 1.5 μm, while their end-cups have been removed by a purification procedure (purity 80–90%). Carboxylic groups are attached both to open ends and sidewalls of SWNTs and their total concentration is about 6% per carbon. The Brunauer–Emmett–Teller (BET) specific surface area of the sample calculated from N_2 adsorption measurements at −196 °C was 73 m^2/g (please note that the sample was outgased at 70 °C, for comparison reasons).

2.2. Preparation of organophilic SWNTs

The chemical attachment of oleylamine was based on a procedure described in details elsewhere [23]. Briefly 30 mg of oxidized SWNTs were dispersed in 5 ml of thionyl chloride and 0.5 ml of dimethyl formamide (DMF) and the mixture heated under reflux for 24 h. The solid material after the reaction was removed by centrifuging and washed with DMF repeatedly. Then chloroform was added and successive centrifuging and removal of the supernatant liquid led to complete removal of DMF. The product was suspended in chloroform and an excess of 1 ml of oleylamine was added and the mixture left to react under stirring for 24 h. The functionalized CNTs were precipitated by ethanol, separated by centrifugation and washed several times with ethanol in order to remove the excess of oleylamine. Finally the product was dried under vacuum for one hour. The concentration of oleylamine on the surface of organophilic SWNTs was 47.5% wt. as determined by thermogravimetric analysis.

2.3. Preparation of hydrophilic SWNTs

30 mg of SWNTs was dispersed in a solution of 30 ml of PPSNa (30% in water) in 20 ml DMF and the mixture was sonicated for 15 min and refluxed overnight. The mixture was diluted with 30 ml of ethanol, and then centrifuged and the residue was separated and dispersed in water by sonication. The suspension was filtered and the water removed by air dry. The concentration of PSSNa on the surface of hydrophilic SWNTs was 42.4% wt.

2.4. Intelligent gravimetric analyser (IGA) measurements

Water (ultra pure Millipore), *n*-hexane (purity > 99%, Merck) and absolute ethanol (Riedel-deHaën) adsorption–desorption isotherms at 25 °C were measured on an Intelligent Gravimetric Analyser (IGA–Hiden Ltd.). An in-house modified arrangement of the IGA vapour admission system allowed in situ distillation of the adsorbate for further purification. The samples of pristine, organophilic and the hydrophilic SWNTs were outgased overnight in 70 °C, under high vacuum (10^{-7} mbar), while proper outgasing was ensured by monitoring the sample weight changes during heating. After cooling to ambient temperature, the sample chamber was immersed in a PID-control circulating bath pre-set to the experimental temperature (25 °C). When the sample temperature measured inside the sample chamber was stabilised, the required pressure values for the equilibrium were defined and vapour was admitted into the balance. During equilibration, pressure was kept constant by means of PID-controlled motor driven inlet and outlet valves. Our gravimetric system allows continuous monitoring of sorption kinetics at each preset pressure point, while in practice an intelligent software code determines equilibrium. For our measurements the system was allowed to wait until sorbing the 99.9% of the total uptake calculated after fitting the kinetic uptake curve. In order to avoid impractically long equilibration times, a maximum equilibration time of 600 min/point was additionally set.

3. Results and discussion

3.1. Characterization of pristine and modified SWNTs

Pristine SWNTs were characterized with TEM microscopy (Fig. 2), IR (Fig. 3) and Raman spectroscopy. The Raman spectra of the pristine sample are characteristic of high quality SWNTs (fewer defects in the structure because of the high ratio of the intensity of the G-band/D-band). The modification of carbon nanotubes was verified by IR spectroscopy and the comparison of the IR spectra indicates clearly the presence of the aforementioned modification. After comparing the IR spectrum of pristine SWNTs with that of organophilic carbon nanotubes, it is evident that the peak corresponding to the aliphatic chain is much stronger due to the presence of oleylamine chain. In the case of organophilic tubes new peaks arise (around 1600 cm^{-1}) which can be attributed to the amide bond formation. A weak peak (around 3030 cm^{-1}) is due to the double bond of oleylamine molecules. The presence of aromatic rings in the case of hydrophilic SWNTs wrapped by the polymer PPSNa is characteristic in 3062 cm^{-1}. Even though the sample was dried under vacuum in 90 °C there is an amount of moisture that was kept by the exceptionally hydrophilic polymer.

3.2. Adsorption properties

3.2.1. Pristine SWNTs

Water is adsorbed in a higher percentage than ethanol and *n*-hexane. This is compatible with the surface chemistry of the pristine samples as the carboxylic acid content is rather high. The free carboxylic groups can strongly interact with water and the hydroxyl group of ethanol through hydrogen-bonding and thus enhance water and ethanol sorption. On the other hand *n*-hexane being totally non-polar can only interact with the carbon surface through Van-der-Waals forces. The sorption isotherms (Fig. 4a) are of type II according to the IUPAC classification, exhibiting a clear BET-like knee at low relative pressures. It should be mentioned that the sorption data of Fig. 4a represent only approximately true equilibrium values. In the case of water and ethanol, equilibrium was not reached even after waiting 600 min at each sorption iso-

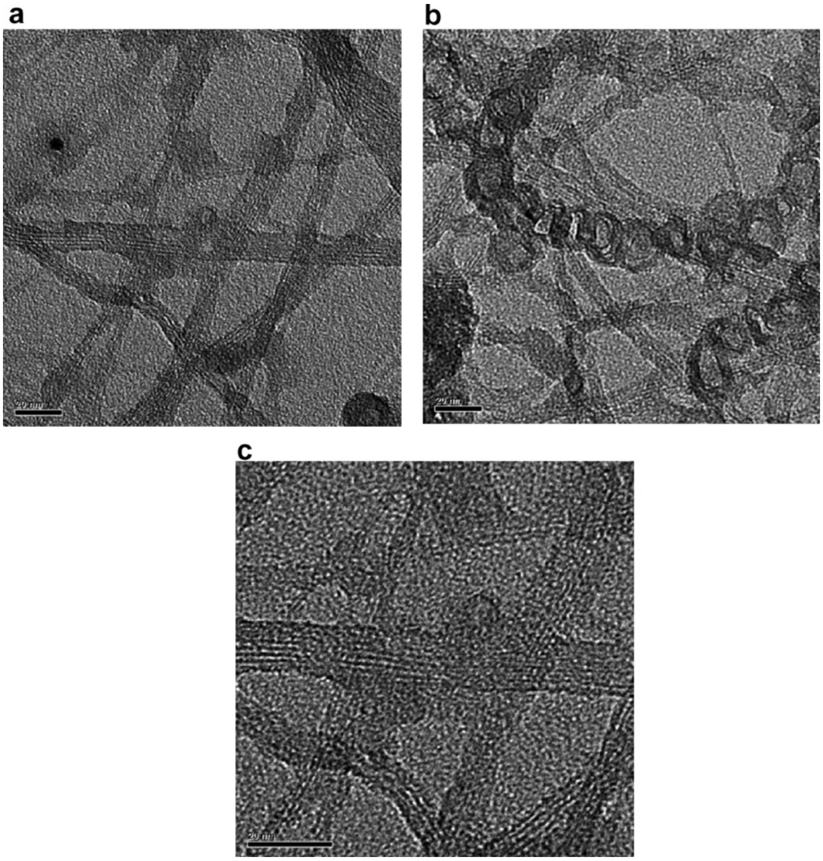

Fig. 2. TEM images (a–c) of the pristine commercial SWNTs that were functionalized in order to prepare hydrophilic and organophilic samples (resolution 20 nm).

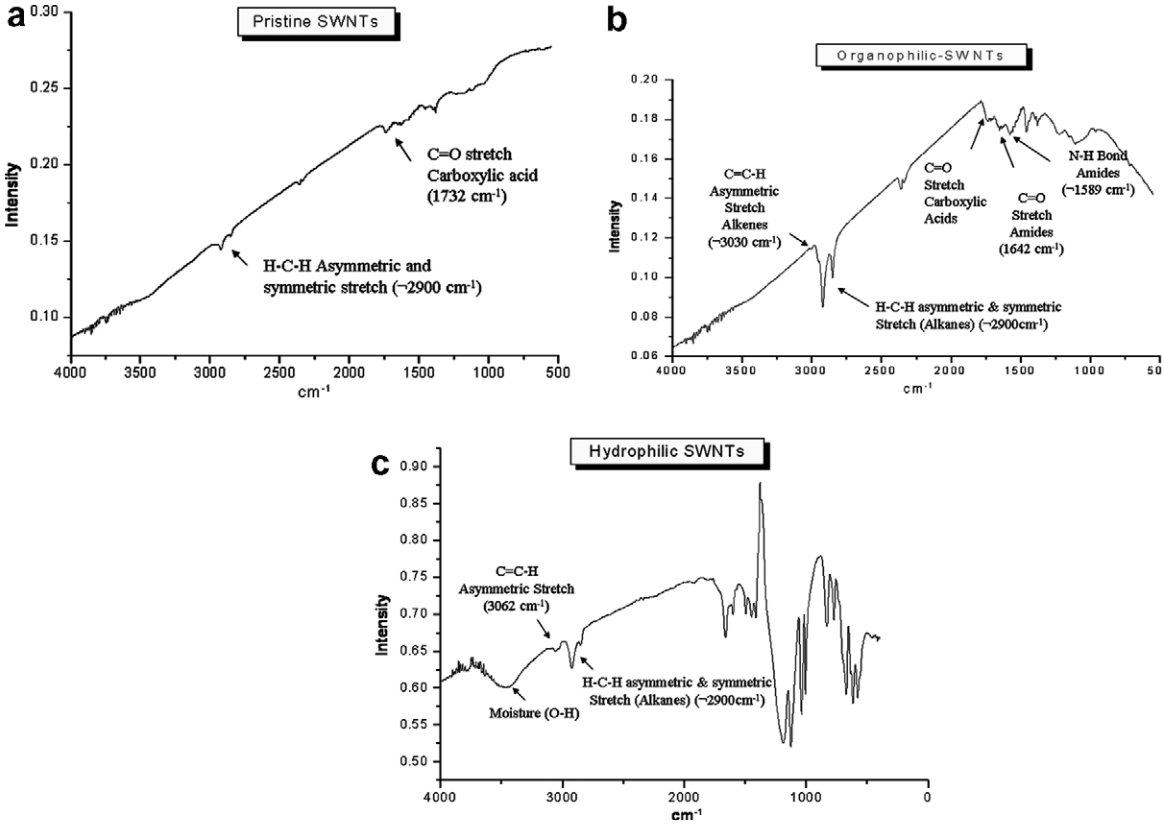

Fig. 3. IR spectra of the pristine (a) and modified SWNTs that illustrate the characteristic peaks for hydrophilic (b) and organophilic (c) samples which verify the aforementioned modification.

therm point, indicating extremely low diffusivities. Such low diffusivities can be attributed to the fact that the entrance of adsorbate molecules inside the nanotubes is hindered not only because of the small size of the tubes but also because the sample has been outgased at a rather low temperature for comparison reasons. The low temperature was applied, since heating above 70 °C would destroy the modified samples as the new entities attached cannot withstand high temperatures. In principle it can be assumed that there are two distinct processes taking place during sample equilibration, (a) adsorption from the vapour phase on the external part of the nanotubes and (b) diffusion of molecules from the vapour phase to sites located in the inner part of the tubes and finally adsorption on these sites. It is concluded that the second process is actually the rate-determining step and being very slow for the reasons explained above, gives rise to the very slow kinetics observed, rendering the system away from equilibrium even after 10 h. On the other hand the *n*-hexane kinetics recorded seem to be much faster (while the amount adsorbed at every point much lower) and the sample was considered at equilibrium after ≈20–30 min. In this case it is concluded that as *n*-hexane is sterically hindered to a much larger extent, adsorption in the inner part of the tube is either too small or too slow, leading in any case to negligible mass change rates (Fig. 5a).

3.2.2. Organophilic SWNTs

For organophilic SWNT sample, *n*-hexane is more adsorbed than water. The isotherms could be characterized as type III, however it can be considered that in this case absorption (mainly of hexane) rather than adsorption may occur (Fig. 4b). This could be attributed to the fact that gas molecules interact with the attached aliphatic chains of oleylamine, while the carbon surface is hardly accessible due to a ‘protective’ hydrocarbon layer that has been developed outside the carbon tube. In this context, *n*-hexane can to a small extent be “dissolved”, while the interaction of ethanol and water with the aliphatic chains sorption is minimal (the amount sorbed is 4–5 times less compared to the pristine sample). The kinetic curves (Fig. 5b) reveal that these samples are also not 100% equilibrated. Nevertheless a quasi-equilibrium state has been reached in less than 40 min while a very slow increase in the amount adsorbed is evident pointing to the existence of a much slower adsorption process. On the other hand the pertinent uptake is so small that the mass increase rate is negligible.

3.2.3. Hydrophilic SWNTs

For hydrophilic SWNT sample a significant enhancement of water sorption is observed, while there is a very small amount of ethanol sorbed and a negligible uptake

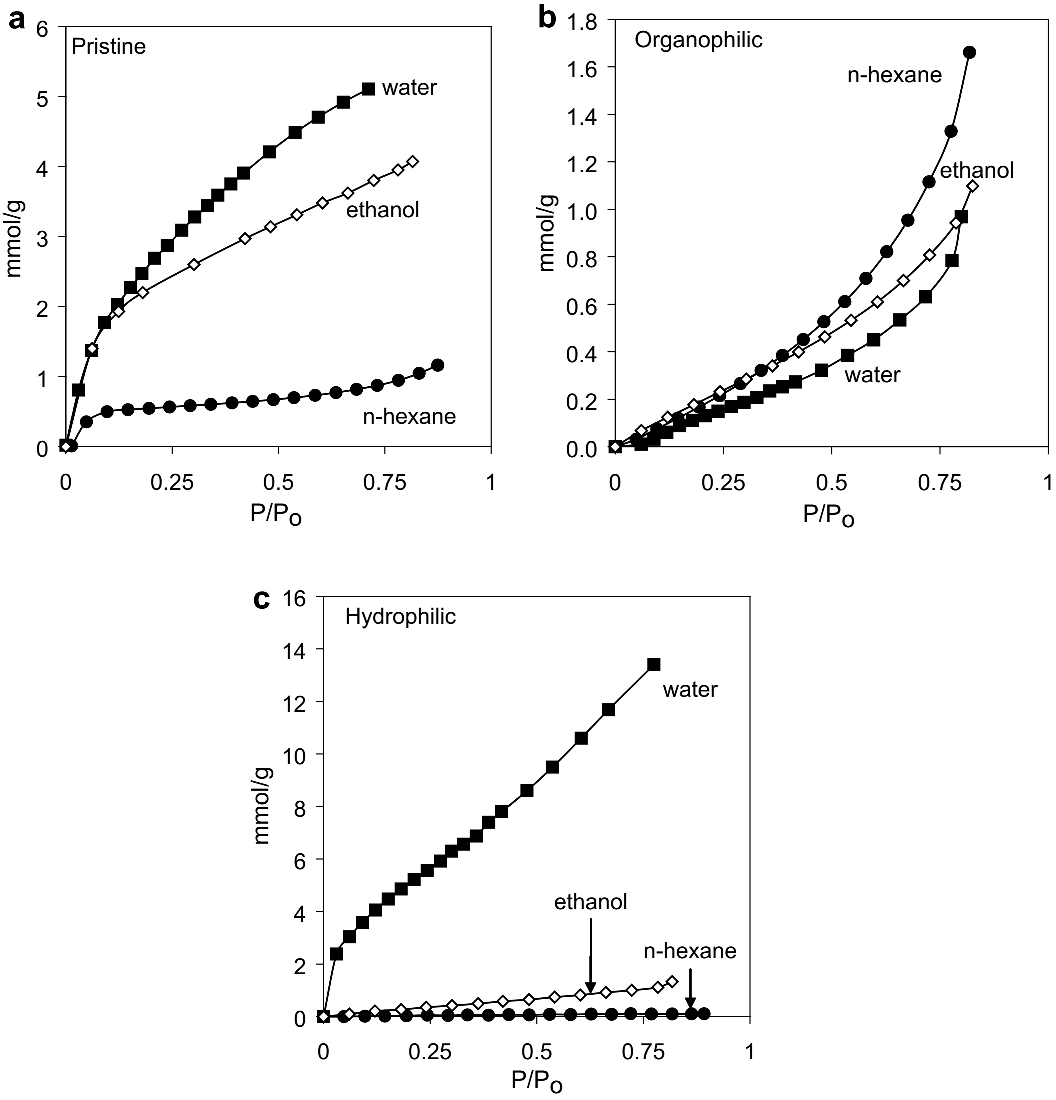

Fig. 4. Adsorption isotherms of three adsorbates which differ in polarity (i.e. water, ethanol and *n*-hexane) for three different samples (a) pristine SWNTs, (b) organophilic SWNTs and (c) hydrophilic SWNTs.

of *n*-hexane. This is attributed to the presence of PSSNa, which strongly enhances hydrogen-bonding and results in more than double adsorbed amount of water than the pristine SWNTs (Fig. 4c). After considering the, at least "partly", hydrophilic nature of ethanol and mainly the ability to participate in H-bonding with PSSNa, one would expect that ethanol sorption would also be enhanced compared to the pristine samples. On the contrary, a severe minimization of the sorbed quantity is observed. This may point to an "exclusion" mechanism, i.e. the ethanol molecules cannot actually penetrate into the tubes. This is also in accordance with the pertinent kinetic data (Fig. 5c), where an extremely slow sorption process is observed. In general the sorption of both hexane and ethanol is extremely slow and is far from equilibrium even after 10 h (Fig. 5c), while water reaches equilibrium (or quasi equilibrium) much faster (faster than 2 h), highlighting the separation capabilities of this sample.

3.3. Comparison

In principle our measurements could allow a detailed analysis of the surface energetics and fully characterize the hydrophilic/hydrophobic character of the samples under consideration. For instance, the integration of the adsorption isotherms expressed per unit surface area up to the monolayer capacity could provide free energy terms, which could consequently be used for a quantification of the hydrophobic/hydrophilic character of the samples [24]. In such a case water and *n*-hexane data would give both polar and Van-der-Waals type free energy term components. There are however, two major problems associated with such an analysis. The first is that modifications have a two-fold effect, i.e. both surface properties and accessibility have been altered. For example our data imply that ethanol molecules can not penetrate in the modified SWNTs and thus a large fraction of the surface area is not accessible.

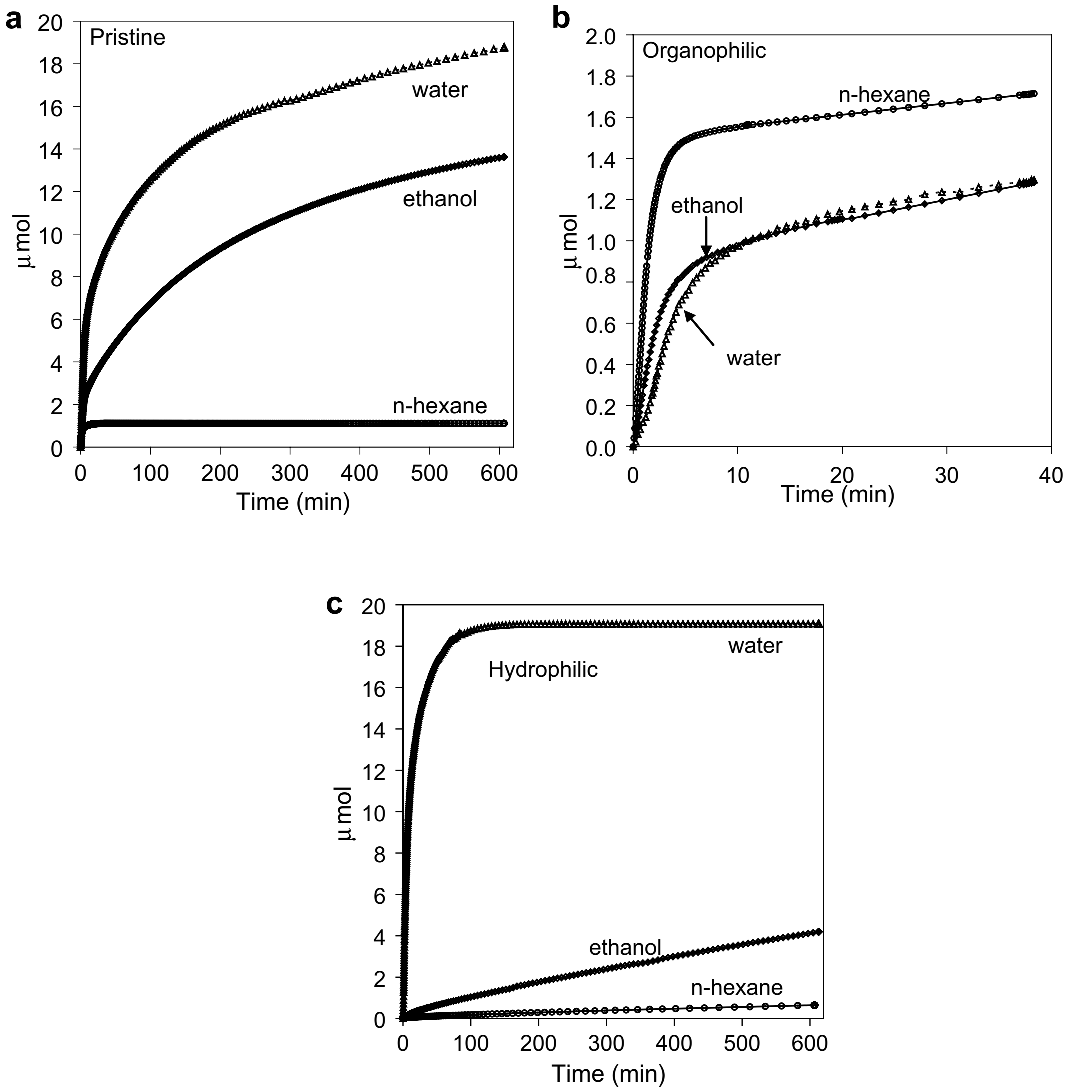

Fig. 5. Kinetic curves which show the uptake versus time for (a) pristine SWNTs, (b) organophilic SWNTs and (c) hydrophilic SWNTs.

The same presumably holds for *n*-hexane and the hydrophilic sample. In this respect the effective area is not the same for the three molecules used. This problem could be overcome by actually determining the effective surface area for each probe (one rather simplistic way would be the calculation of BET surface areas based on the isothermal data and molecular dimensions). Nevertheless, there is a second more severe reason which hinders the application of such an analysis. As explained above the measured isothermal data do not refer to true equilibrium values. The isotherms measured are actually, a convolution of the thermodynamics in the gas–solid interface (surface hydrophilicity/hydrophobicity) and the effective process kinetics (molecular diffusivity and steric hindrance but also sorption rates). In all cases equilibrium has not been reached, while in several cases (ethanol and *n*-hexane in hydrophilic SWNTs) the kinetic histories show that the sorbent-sorbate system is very far from equilibrium. In this respect, a detailed thermodynamic analysis of our results would be at least doubtful, if not completely out of the context, as the ratio between polar and Van-der-Waals forces would be time dependent (different equilibration times would produce different results). It should however be mentioned even though the results are not true equilibrium isotherms, they are true uptake values and in this framework they clearly indicate the separation potential of the samples. Unfortunately, the contributions of surface forces and kinetics are indistinguishable, however longer measurements until equilibrium (much more than 600 min/point) would be impractical on one hand and not indicative of real separation process on the other. Based on the above the terms hydrophilic and organophilic are and should only be used in a qualitative manner and pertain rather to a classification of the sample performance than to an actual description of the surface forces. Likewise, in the following, selectivity should be considered rather as overall 'process selectivity' and not as a surface energy term, since the separation potential is based on both kinetics and thermodynamics.

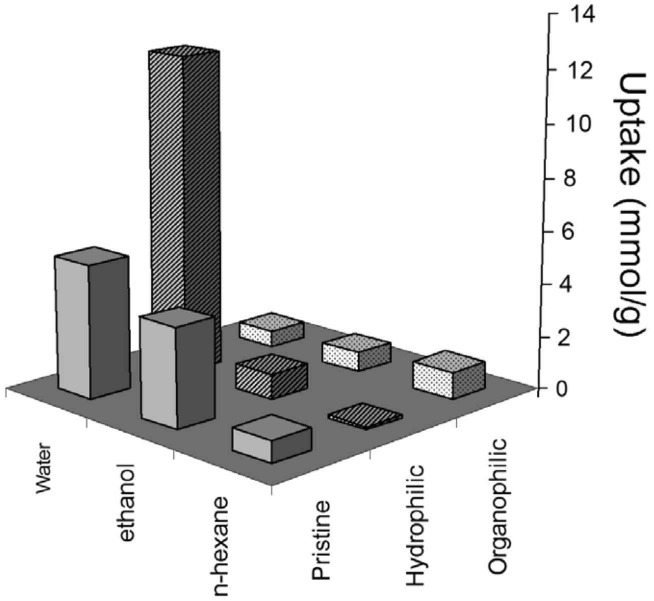

Fig. 6. Bar chart indicating the impact of functionalization on the uptake of the vapours.

As it can be seen by the isotherms (Fig. 4a) the pristine sample is inherently water selective. The modifications result in either a significant enhancement of this process selectivity (hydrophilic SWNTs) or in the reversal (organophilic SWNTs). The bar chart of Fig. 6 shows the uptakes of different vapours at $P/P_0 = 0.7$ and clearly demonstrates that although the general pattern is the same in the case of pristine and hydrophilic samples, a sharp enhancement in the uptake of water coupled by a respective reduction of the uptake of *n*-hexane is observed. This sequence is reversed in the case of the organophilic sample where *n*-hexane is adsorbed at a higher percentage than water (Fig. 6). Moreover, ideal water/*n*-hexane selectivities of equimolar mixtures have been calculated as the ratio of individual uptakes for the pristine and modified samples and are compared in Fig. 7. As seen in Fig. 7 the pristine sample has a selectivity value below 10, while the selectivity of the hydrophilic sample exceeds 120 (and is more than 200 at $P/P_0 = 1$). It should be pointed out that if we additionally consider competitive adsorption phenomena as well as the significant differences in the kinetic behaviour of water and *n*-hexane, it is anticipated that the real mixture selectivity of the sample (especially for short times, e.g. below 100 min) will be much more than the ideal one (Fig. 5c). This process selectivity is fully reversed in the case of organophilic sample, which are *n*-hexane selective (water/*n*-hexane <1) (Fig. 7).

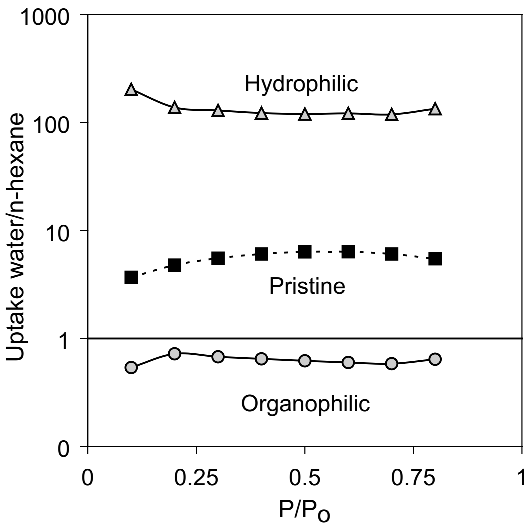

Fig. 7. Comparison of the ideal selectivity water/*n*-hexane for the three samples.

4. Conclusions

The very limited SWNTs solubility in common solvents is a serious problem that severely hampers their use for the fabrication of advanced composite materials. This roadblock can be alleviated through chemical modification or functionalization of their surfaces. In this work, we report the modification of commercial SWNTs with high carboxylic acid content, which results in the change of their solubility properties rendering them organophilic (with oleylamine), or hydrophilic (wrapping of the SWNTs with PSSNa). The modification of carbon nanotubes was verified by IR spectroscopy, while their sorption properties were studied by using sorption of different polarity vapours (water, ethanol and *n*-hexane).

The sorption results reported in this study are not true equilibrium values, however confirmed that the sorption properties of SWNTs could indeed be tailored to a significant extent. Specifically, the functionalised samples revealed exactly opposite overall process selectivity profiles, both of which were different from that of the pristine sample. For example the organophilic SWNTs are *n*-hexane selective (*n*-hexane/water ≈2 at $P/P_0 = 0.7$), adsorbing ten times higher amount of *n*-hexane than the hydrophilic ones ($P/P_0 = 0.7$). On the other hand hydrophilic SWNTs are highly water selective (water/*n*-hexane ≈120 at $P/P_0 = 0.7$) and adsorb water at least twenty times higher ($P/P_0 = 0.7$) than the organophilic sample. It should nevertheless be explicitly mentioned that the separation abilities of the modified samples are based on a combination of surface chemistry properties and steric hindrance effects.

Such chemical modifications of SWNTs are very important in a series of applications. The most obvious one would be the development of novel systems (membranes and/or adsorbents) with enhanced selectivity for a variety of applications in separations of hydrophilic/hydrophobic molecules. This may lead to the reduction of the cost of some processes as e.g. the separation of water/ethanol azeotropic mixtures, removal of hydrophobes in aqueous environment, etc. Additionally, rendering SWNTs soluble in different media is very important in using them as nanoadditives. For instance SWNTs could be used in several nano-composite polymeric materials (e.g. in order to enhance their mechanical strength), without any restriction in the choice of the polymeric material or the solvent to be used. Finally since these modifications lead to satisfactory dispersion of the nanotubes both in polar and non-polar media they can render SWNTs useful as versatile precursors to polymer materials with distinctive mechanical and electrical properties, as new ligands for metal complexation in heterogeneous catalysis, removal of volatile organic compounds (VOCs), slow release of hydrophobic molecules (e.g. drug delivery) in aqueous systems, etc.

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