INORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2018, **5**, 1978

HBPEI-grafted carbon nanotubes for the effective retention of Pd^{2+} and Pt^{2+} through complexation†

Víctor K. Abdelkader-Fernández, ‡§[a] Francisco Morales-Lara,¶‡[a] Mª Dolores López de la Torre, [b] Manuel Melguizo, [b] F. Javier López-Garzón, [a] María Domingo-García[a] and Manuel Pérez-Mendoza *[a]

Received 8th April 2018,
Accepted 21st June 2018

DOI: 10.1039/c8qi00320c

rsc.li/frontiers-inorganic

Hyperbranched poly(ethyleneimine) (HBPEI) molecules in solution present high capacity to form stable complexes with transition metal ions due to the large number of amino groups ready to form chelates. We grafted HBPEI molecules to a multi-walled carbon nanotube (MWCNT) surface through covalent bonding, preparing solid hybrids which retain the chemical properties of the free poly-alkylamine molecules. In this way, we are able to transfer the complexation capacity of such molecules to a solid material adequate to act as a high-capacity sorbent for metal transition ions. We tested the HBPEI/MWCNT hybrids for the retention of Pd^{2+} and Pt^{2+} and the retention values obtained are much larger than those previously reported with fast retention kinetics. The kinetics and the XPS analysis of the metal ion/HBPEI/MWCNT ensemble indicate that the retention takes place through the formation of chelates with two or three nitrogen atoms and with Cl^- anions as co-ligands. Moreover, the results allow us to tune the metal loading on the hybrids by controlling the solution conditions. This is important because the XPS valence band analysis demonstrates that metal complexation directly modifies the electronic behaviour of the carbon nanotubes, which supports the stable covalent bond between HBPEI molecules and MWCNT and opens the possibility for tuning the electronic properties of the tubes.

Introduction

The synergy produced between carbon nanomaterials and chemical functions grafted on their surface can substantially modify their properties and widen the range for potential applications.[1–10] The attachment of the guest function merges the properties of carbon nanotubes with the intrinsic characteristics of the function. The link through a covalent bond adds stability to the hybrid materials due to the strength of the union formed. Such stability is a key factor for many applications.[2,6,11,12]

Among the chemical functions that can add chemical versatility to carbon nanomaterials, the grafting of amine groups is interesting as they can modify the solubility in different media and change the acid–base character of the materials.[7,11,13] Moreover, the good complexing behaviour of the amino groups and their affinity towards certain metal ions can be an additional advantage of decorating carbon nanomaterials with these nitrogen functions, as they can behave as poly-chelatogens.[14–17]

Polymeric amines offer an interesting approach for such functionalization as a large number of amine functions can be grafted through a single chemical bond. Hyper-branched polyethyleneimines (HBPEIs) are a clear example as they are water soluble homopolymers with a large proportion of primary (terminal) amines. In that respect, the HBPEIs are more interesting than linear polyethyleneimines (LPEIs), which have only two terminal amino groups. The presence of multiple primary-amine groups can be ideal for the covalent grafting to carbon materials. The polyamine molecule can be linked to the carbon surface through several bonds providing more stable HBPEIs/hybrid materials.[14]

Several procedures have been proposed for the functionalization of carbon materials with amine functions.[11,15,18,19] Many of them are based on the reaction with electrophilic groups introduced on the surface of the material through a primary functionalization (with a strong oxidant to increase the concentration of oxygen containing groups, for example). This several-step approach involving a primary functionali-

[a]*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain. E-mail: mjperezm@ugr.es*
[b]*Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain*

†Electronic supplementary information (ESI) available: Supplementary experimental data. See DOI: 10.1039/c8qi00320c

‡These authors have contributed equally to this work.

§Current address: Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre, s/n, 4169-007 Porto, Portugal.
¶Current address: Istituto Italiano di Tecnologia (IIT), Nano Carbon Materials, Via Livorno 60, Turin, Italy.

zation is necessary in order to increase the reactivity of the carbon surface towards the amine compounds. Other strategies are based on the intrinsic reactivity of the amines towards 5-carbon-atom rings, which are present as common defects in bent areas of graphene-based structures. In these cases, amine functionalization is therefore usually restricted to dangling atoms at the end of the structures, defects on the walls and closed ends of carbon nanotubes. Our research group successfully addressed the functionalization of MWCNT and other carbon materials with HBPEIs following different strategies: (i) a methodology based on the oxidation, esterification and reaction with HBPEIs;[14] (ii) non-catalyzed direct reaction[20] and (iii) CuI catalyzed reaction with HBPEIs.[20]

All of them give high degrees of functionalization, but the metal-catalyzed amination of MWCNT is able to fix large amounts of nitrogen in a single-step process using mild conditions. This novel strategy allows also for a functionalization that is independent of the amount of defects, as the reaction takes place in the sp^2 carbon atoms of the graphenic domains.[20] The main goal pursued with all the previously mentioned functionalization methodologies is to effectively transfer the chemical properties of the polyamines to the solid material (especially those related to their behaviour as polychelatogens) obtaining stable MWCNT/HBPEI hybrids with enhanced properties. The fact that the complexing capacities of HBPEIs can be successfully transferred to the solid carbon nanomaterials opens up new possibilities to design selective scavengers for the removal of certain metal ions from solution. We reported[14] some preliminary results of the retention of Ni^{2+} ions by the prepared hybrids as a proof of concept of the possibilities of our materials. In this work, we present an exhaustive analysis of the capabilities of the HBPEI/MWCNT hybrids for the retention of precious metal ions such as Pd^{2+} and Pt^{2+} (Fig. 1). The recovery of such ions is very important in many industrial applications due to the added value of these metals. The results show that the retention capacities towards both metal ions are well above the highest reported to date.[16,21,22] A detailed description of the retention process, and the factors that influence the formation of the complexes, is presented. The results clearly show that the complexing properties of the polyamines can successfully be transferred to carbon nanomaterials opening new possibilities for the decoration of such materials with metals.

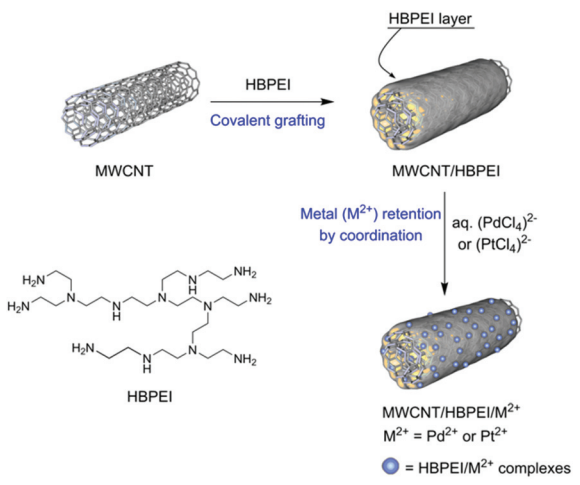

Fig. 1 Methodology to obtain MWCNT/HBPEI hybrids, and the capture of Pd^{2+} and Pt^{2+} by complexation.

Experimental

Commercial CVD multi-walled carbon nanotubes (NC-3100) from Nanocyl and a hyperbranched polyethyleneimine (HBPEI) from Sigma-Aldrich were used to prepare these hybrid materials. The MWCNT have an average external diameter of 9.5 nm and a mean length of 1.5 μm, and the HBPEI has an average molecular weight (M_n) of 1800 g mol^{-1}. The MWCNT/HBPEI hybrid materials were prepared by three different procedures, as described in former studies.[14,20] The first one consists in the direct reaction of the HBPEI with the pristine MWCNT. The sample so obtained is mentioned in the second column of Table 1 as (1). The second procedure consists in the reaction of the amine functions of the HBPEIs with carbonyls and carboxylic anhydrides fixed to the MWCNT surface by previous oxidation (samples marked as (2) in Table 1). The third method implies the CuI catalyzed reaction of pristine MWCNT with the HBPEI (samples marked as (3) in Table 1).

The names of the hybrids obtained by these procedures are mentioned in the first column of Table 1. In the label of the MWCNT/HBPEI hybrids, HBPEI is replaced by the percentage of polyamine in the hybrid. For example, the MWCNT/11.9 label denotes a hybrid having 11.9% (wt/wt) of HBPEI. Table 1 also contains the amount of HBPEI (third column) and the nitrogen content of the hybrids. The amounts of nitrogen of these hybrids are really large although smaller than those reported for the covalent attachment of a 25 000 Da HBPEI on nanocarbons.[23]

We analyzed the chemical behavior of the MWCNT/HBPEI hybrids in aqueous solution to compare with that of the free HBPEI. The aim is to check if the chemical characteristics of the HBPEI are transferred to the MWCNT/HBPEI hybrids. This is a cornerstone of this work, as the hybrids must retain the

Table 1 Hybrid materials

MWCNT/HBPEI hybrid	Synthesis approach	HBPEI[a] (%) (wt/wt)	N^a (%) (wt/wt)	N^b (at %)
MWCNT/8.1	(1)	8.1	2.6	3.3
MWCNT/11.9	(2)	11.9	3.9	5.4
MWCNT/8.3	(2)	8.3	2.7	4.2
MWCNT/8.6	(3)	8.6	2.8	3.3
MWCNT/11.7	(3)	11.7	3.8	5.6
MWCNT/18.2	(3)	18.2	5.9	7.7
MWCNT/22.9	(3)	22.9	7.5	8.3
MWCNT/31.0	(3)	31.0	10.1	11.0

[a] Measured by CNHS-elemental analysis. [b] From XPS spectra.

acid–base and complexing abilities of the HBPEI in order to capture the metal ions. The set-up to determine the acid–base characteristics consists of an automatic device equipped with a METHROM glass-calomel electrode (titration electrode), a METHROM 765 Dosimat autoburette (0.001 ml dose accuracy), a METHROM 713 pH-meter control unit and a SELECTA Frigiterm 6000382 thermostatic bath. The titrations of the HBPEI/H^+ solutions and of MWCNT/HBPEI/H^+ were carried out under a nitrogen atmosphere at a molar concentration of 6×10^{-3} M. $N(CH_3)_4Cl$ was used as the electrolyte to fix the ionic strength to 0.1 M in chlorides. The starting pH was set at 2.5 and the titrating agent was $N(CH_3)_4OH$. The coordination capacity of the HBPEI and of the MWCNT/HBPEI hybrids with Pd^{2+} and Pt^{2+} was studied in the same experimental set-up used for the acid–base titrations.[24]

As mentioned, the aim of this work is to use the MWCNT/HBPEI hybrids to capture the largest possible amounts of Pd^{2+} and Pt^{2+} by complexation (*cf.* Fig. 1). For this purpose, the complexation kinetics for the retention of both ions by the MWCNT/HBPEI hybrids was obtained. Typically, 25 mg of the MWCNT/HBPEI hybrid material were added to a 2×10^{-3} M aqueous solution of K_2PdCl_4 (Alpha Aesar) and 1×10^{-3} M of K_2PtCl_4 (Alpha Aesar). The ionic strengths of the solutions were kept at 0.1 M of KCl and KNO_3 for palladium and platinum, respectively. The initial pH was set to 5 and 6 for Pd^{2+} and Pt^{2+} solutions and the temperature was set to 25 °C. The amounts of both ions captured by the hybrids were determined by analyzing the initial and final concentrations of the solutions. UV-Vis equipment (Lambda 25 from PerkinElmer) and ICP-MS apparatus (Series 7500 from Agilent) were used for palladium and platinum respectively. The experimental data were fitted to a pseudo-second order kinetic model:

$$dq_t/dt = k(q_e - q_t)^2 \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{kq_e{}^2} + \frac{t}{q_e} \quad (2)$$

In these equations, k is the rate constant, q_e the amount of captured metal at equilibrium and q_t the amount of metal retained after a time t.

The results of the kinetics allowed us to obtain the adsorption isotherms (by complexation) of both metal ions in a concentration ranging from 0.05×10^{-3} to 3.3×10^{-3} M. The rest of the experimental conditions to obtain the adsorption isotherms were the same as the kinetics, and the equilibrium times were set to 48 h.

The characterization of the metal loaded hybrids was carried out by XPS and electron microscopy. The XPS spectra were acquired in a Kratos Axis Ultra DLD spectrometer. A monochromatic AlK_α radiation in constant analyser energy mode with pass energies of 160 and 20 eV (for the survey and high resolution spectra, respectively) was used. The C 1s transition at 284.6 eV was used as the reference to obtain the binding energies of heteroatoms. A HAADF FEI TITAN G2 microscope with resolutions of 8 Å in TEM mode and 1.4 Å in STEM mode was used for imaging the hybrid materials as well as for the EDX microanalysis and mappings. The microscope was operated with a working tension of 300 kV. Besides, images, EDX microanalysis and mappings were also obtained using a SEM microscope Zeiss SUPRA40VP.

Results and discussion

Experimental data on the characteristics of the MWCNT/HBPEI hybrids (*i.e.* thermograms, thermal desorption profiles, and X-ray photoelectron spectroscopy (XPS) spectra) are supplied in the ESI, 1–3.† These data together with others already reported support the fact that the HBPEI is covalently bonded to the MWCNT[14] and homogeneously distributed on the surface of the nanotubes, as clearly shown by the STEM nitrogen map in Fig. 2.

Table 2 shows the values of the acid–base equilibrium constants of the free polyamine in aqueous solution and those of a selected hybrid (L in the compounds of Table 2 stands for HBPEI). Both HBPEI and MWCNT/11.9 have the same type of acid–base equilibrium. The general decrease of the constants in the hybrids is due to the decrease of the number of protonable amino groups as a consequence of the covalent bond between the HBPEI and the MWCNT.

The fact that the acid–base behavior of both the free HBPEI and the hybrids is very similar suggests that the hybrids must keep not only the acid–base characteristics but also their complexing properties. This is a key factor considering the aim of this work, *i.e.* to obtain solids able to capture large amounts of Pd^{2+} and Pt^{2+}.

Thus, the complexation behaviour of the hybrids towards metal ions is expected to be very close to that of the free poly-

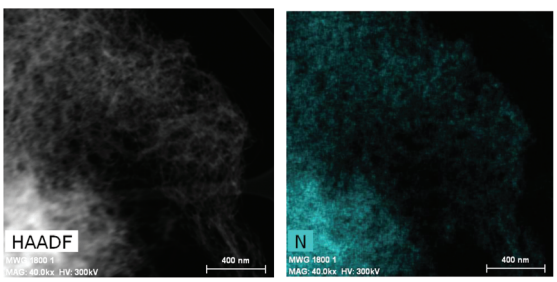

Fig. 2 STEM image (left) and nitrogen map (right) of sample MWCNT/31.0.

Table 2 Acid–base equilibria and values of the constants

	log K	
Acid–base equilibrium	HBPEI	MWCNT/11.9
$H^+ + L_2 \leftrightarrow [HL_2]^+$	12.06 ± 0.02	11.05 ± 0.07
$H^+ + L \leftrightarrow [HL]^+$	9.58 ± 0.05	8.11 ± 0.03
$H^+ + 2[HL]^+ \leftrightarrow [H_3L_2]^{3+}$	10.54 ± 0.06	8.93 ± 0.07
$H^+ + HL^+ \leftrightarrow [H_2L]^{2+}$	6.67 ± 0.06	5.63 ± 0.03
$H^+ + 2[H_2L]^{3+} \leftrightarrow [H_5L_2]^{5+}$	4.33 ± 0.02	5.89 ± 0.05

amine in solution. The reactivity plot of a Pd^{2+} aqueous solution with the free HBPEI is shown in the ESI† and the species distribution obtained from this plot is shown in Fig. 3.

The most abundant species are complexes with a partially protonated or deprotonated polyamine as they represent more than 90% of the species. Moreover, it is evident that the complexes are mono-nuclear with a stoichiometry of $L/Pd^{2+} = 1/1$. Thus, if the preference of Pd^{2+} for square-planar geometries is considered, the coordination of the HBPEI must take place as a mono-, bi- or tridentate ligand in the complexes $[Pd(Cl_x)H_2L]^+$ where $x = 1–3$.

If the complexation interaction of the HBPEI with the metal ions mentioned above is retained after the grafting to the MWCNT surface, MWCNT/HBPEI hybrids must present a similar capacity to capture such metal ions by coordination.

The kinetics and retention isotherms of Pd^{2+} and Pt^{2+} by the HBPEI/MWCNT hybrids and by the pristine MWCNT were compared to get an insight into the process. Fig. 4a shows the kinetics of the pristine nanotubes and those of a selected hybrid (MWCNT/11.9) for 1×10^{-3} M solutions of $PdCl_4^{2-}$ and $PtCl_4^{2-}$. It is evident that the hybrid captures much larger amounts of Pd^{2+} (red line) and Pt^{2+} (black line) than the original nanotubes (green and yellow lines, respectively), while the oxidized MWCNT retain almost the same amount of metal ions than the pristine tubes (see S7 in the ESI†). Therefore, the metal retention is due to the coordination of the HBPEI with the metal ions.

The experimental kinetic values fit a pseudo-second order equation (Fig. 4b and eqn (2), *cf.* Experimental section), thus indicating that the capture of the metal ions is caused by a chemical process, *i.e.* by coordination at the external surface of the hybrid, being a purely surface phenomenon. Moreover, a faster and larger retention for Pd^{2+} than for Pt^{2+} is observed. The isotherms are shown in Fig. 4c, which indeed also show the same trend as in Fig. 4a. The larger retention values for Pd^{2+} are in agreement with the values of the stability constants of the amine complexes of these ions, larger for Pd^{2+} than for Pt^{2+}, as reported in the literature.[25] Fitting the isotherm data to the Langmuir equation (Fig. 4d) allows us to obtain the maximum retention amount of ions by the hybrids: 1.16 and 0.97 mmol g^{-1} for Pd^{2+} and Pt^{2+}, respectively.

Fig. 5 shows the survey XPS spectra of the nanotubes before the covalent attachment of the HBPEI (black), of a hybrid (green) and after the capture of Pd^{2+} and Pt^{2+}. The presence of both metals is evident in the hybrids, as well as nitrogen and chlorine. This suggests that, in addition to the metal coordination by the HBPEI, chlorine also acts as a ligand in the coordination compound formed by both metals. It is necessary to remark that $PdCl_4^{2-}$ and $PtCl_4^{2-}$ salts were used to prepare the solutions of the metal ions.

The hyperbranched nature of the amine groups able to coordinate the metal ions in the HBPEI must provide a homogeneous distribution of Pd and Pt on the surface of the solid material. The images of the EDX maps in Fig. 6, obtained by electron microscopy, clearly support this statement. Moreover, the homogeneous distribution of chlorine also supports the above comment about the role of chlorine as a ligand.

The plots in Fig. 7 show the relationships between the content of nitrogen and the maximum amount of metal captured by the hybrids for different amounts of HPBEI. The excellent fittings found in these plots are clear evidence supporting the finding that the retention of the metal ions by the

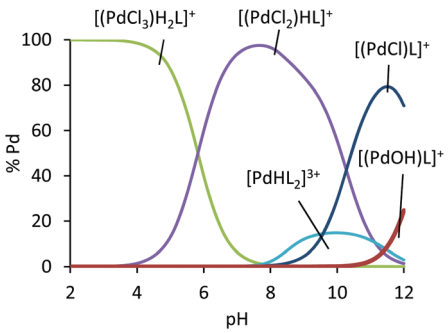

Fig. 3 Species distribution obtained from the reactivity plot of Pd^{2+} aqueous solution and the free HBPEI (L stands for HBPEI).

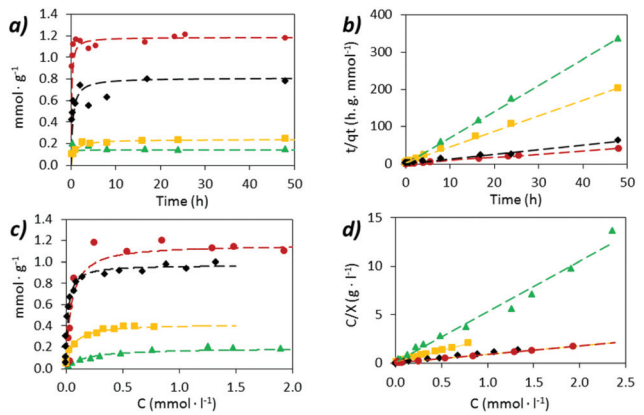

Fig. 4 (a) Retention kinetics, (b) fitting the kinetic values to a pseudo-second order equation, (c) retention isotherms and (d) fitting the retention data to the Langmuir equation, of Pd^{2+} and Pt^{2+}. Green and yellow marks belong to pristine MWCNT for Pd^{2+} and Pt^{2+}, respectively. Red and black marks belong to the MWCNT/11.9 hybrid for Pd^{2+} and Pt^{2+}, respectively.

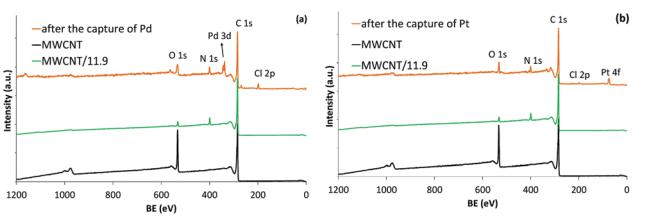

Fig. 5 XPS survey spectra showing the presence of Pd (a) and Pt (b) after the capture of both metals by the hybrids.

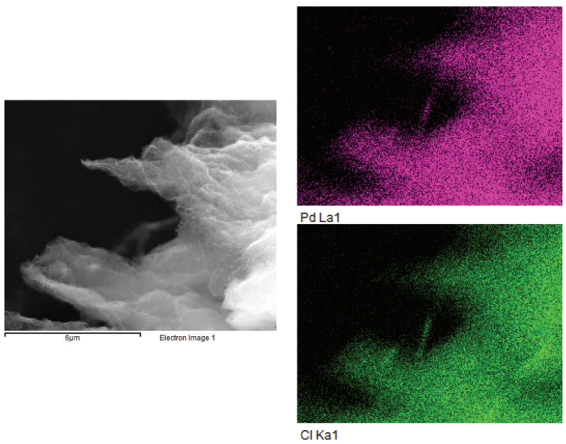

Fig. 6 SEM image and EDX maps of MWCNT/11.7 after the capture of Pd^{2+}.

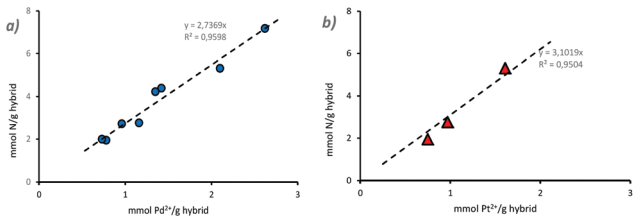

Fig. 7 Relationship between the nitrogen content of the hybrid and the amount of metal ions captured: (a) Pd^{2+} and (b) Pt^{2+}.

MWCNT/HBPEI hybrids is produced through complexations with the amine groups of the HBPEI.

The analysis of the high resolution XPS spectra (between 347 and 333 eV for the Pd 3d region and between 68 and 80 eV for the Pt 4f) of the MWCNT/HBPEI/M (M = Pd^{2+} or Pt^{2+}) materials (*cf.* ESI†) points out that the vast majority of both metals are in the form of divalent ions after the retention.

To establish how both metal ions appear in the hybrids it is necessary to consider that Pd^{2+} and Pt^{2+} have a preference for coordination compounds with a square planar stoichiometry. Moreover, the species distribution plots (Fig. 3) point out that the species are mono-nuclear (L/Pd^{2+} = 1/1). Thus L has to behave as a mono-, bi- or tridentate ligand depending on its degree of protonation. Furthermore, the structure of the HBPEI is polymeric and consists of ethylenediamine fragments (*cf.* Fig. 1), in which every two consecutive nitrogen atoms are always in 1,4 relative position, bound through flexible ethylene fragments.

These fragments are ideal for the formation of five-membered chelates (involving two consecutive nitrogen atoms) or even double five-membered chelates involving three consecutive nitrogen atoms bonded to a single metal ion.[26,27] This implies a nitrogen/metal (N/M, M = Pd^{2+} or Pt^{2+}) atom relationship ≥2 for the MWCNT/HBPEI/Pd hybrids if two or three nitrogen atoms form the chelate (the other positions being occupied by chloride).

The experimental average N/M ratios obtained from the slopes of Fig. 7 are 2.7 and 3.1 for Pd^{2+} and Pt^{2+} respectively, which suggests that between two and three nitrogen atoms are coordinated to the metal. In addition, the XPS analysis of the Cl content of a set of Pd-containing hybrids reveals an excellent linear correlation between the amount of Cl, as chloride, and the amount of Pd^{2+} in the hybrid (Fig. 8).

The value of the slope of that linear correlation, 1.99, indicates a round value of 2 chloride ligands for each Pd^{2+} ion, which not only accounts for the electroneutrality of the Pd^{2+} complexes, but also provides key information to ultimately propose a rational model for the complexation of the Pd^{2+} ions by the HBPEI of the hybrids (Fig. 9). Thus, at least two chloride ions of the coordination sphere of the initial $(PdCl_4)^{2-}$ were replaced with two HBPEI nitrogen atoms forming chelate complexes.

The participation of hydroxide ions as ligands in the Pd^{2+} complexes is practically discarded taking into account the potentiometric titration data of the Pd^{2+}–HBPEI complexes in aqueous solution (*cf.* ESI†). These data point out that hydroxide complex species only start forming at pH values over 10, really far from the acidic conditions that we used to prepare the Pd-contaning hybrid materials.

For the hybrids containing Pt^{2+}, the plot of the nitrogen content *versus* the retention capacity of Pt^{2+} (Fig. 7b) shows a linear trend with a N/Pt relationship of 3.1. Nevertheless, no

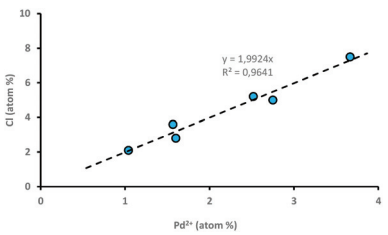

Fig. 8 Amount of chloride *versus* Pd^{2+} for MWCNT/HBPEI hybrids.

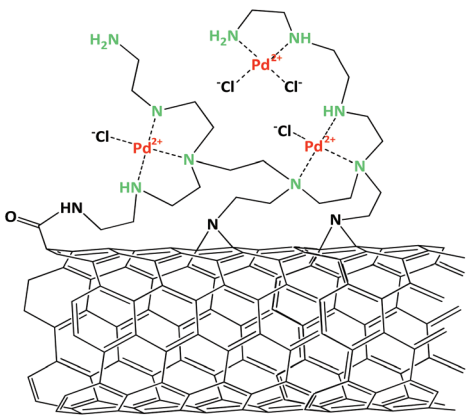

Fig. 9 The coordination of Pd^{2+} by the HBPEI on the surface of the carbon nanotubes.

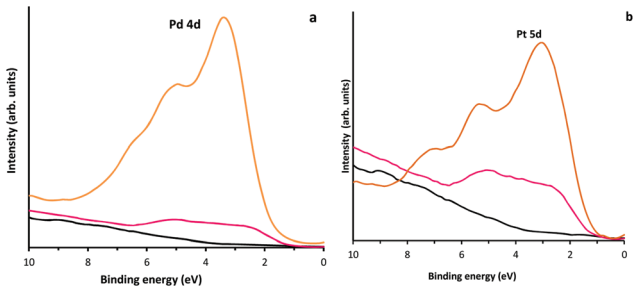

Fig. 10 XPS spectra in the low binding energy region of the original MWCNT and of the MWCNT/11.9 hybrid before and after the capture (orange line) of Pd and Pt, (a) and (b), respectively.

good relationship between the chloride and Pt^{2+} contents is found, though there is a general tendency of an increasing chloride content as the Pt^{2+} content rises (*cf.* ESI†). Then, a clear complex model cannot be proposed on the basis of the experimental data in this case, although a similar behavior to that observed for Pd^{2+} is expected owing to the parallel complexing abilities of these two metal ions.[28]

The fit of the isotherm data to the Langmuir equation (Fig. 4d) also allows us to determine the initial concentration of ions needed to prepare MWCNT/HBPEI hybrids containing the desired amount of ions. In other words, we can prepare MWCNT/HBPEI hybrids loaded with any selected amount of ions below the maximum retention capacity of the hybrid by tuning the initial ion concentration. Thus, we used this procedure to obtain hybrids containing amounts of Pd^{2+} and Pt^{2+} in a wide range up to values as large as 2.60 and 1.61 mmol g^{-1} respectively. These values represent 22.3 and 31.5% (wt/wt) of Pd^{2+} and Pt^{2+} in the hybrids and are much larger than those previously reported, and even larger than those for the commercial sorbents used to recover these metals.[21,22] We have also reported[16] hybrid materials based on active carbon and a polyamine with high capacity to capture Pd^{2+} but the amounts are smaller than these obtained with the hybrids presented in this work. Thus, these carbon nanotube based hybrids can be envisaged as excellent materials to recover both Pd^{2+} and Pt^{2+} from solution.

Moreover the XPS spectra in the valence band region of the hybrids (after capturing the metal ions) show interesting features. Fig. 10 shows that the spectrum of the parent nanotubes presents meaningful photoelectron emission only at binding energies larger than 6 eV. This points to a non-conducting material. The covalent attachment of the HBPEI to the nanotubes results in a small photoemission in the range between 2 and 6 eV. Nevertheless, after the metal capture there is a drastic increase of photoemission close to 2 eV which matches a semiconducting behavior. Thus the capture of the metal ions by coordination alters the electronic behaviour of the hybrid.

Conclusions

The similar measured constants of the acid–base equilibria and species distribution of both the free and grafted HBPEI molecules demonstrate that the complexing capabilities of the poly-alkylamines can be effectively transferred to the hybrid materials. These properties can therefore be exploited to selectively capture metal ions from solutions.

The kinetics and retention isotherms of Pd^{2+} and Pt^{2+} by the HBPEI/MWCNT hybrids show a much higher retention capacity for both ions than the pristine MWCNT. The pseudo-second order kinetics indicates that the retention is produced through coordination at the external surface of the hybrids, not limited by diffusion phenomena. The relative amounts retained can also be related to the stability constants of the amine complexes of the ions.

XPS studies of nitrogen and chlorine in the form of chloride contents lead to the conclusion that chlorine also forms a part of the complexes as a co-ligand, with both metals staying as divalent ions. Therefore, the retention must take place through a coordination forming square-planar complexes by substituting at least two chlorine atoms of the initial $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ ions.

Finally, it is remarkable that this methodology allows loading the hybrids with a previously desired amount of metal ions. We used this procedure to obtain hybrids containing amounts of Pd^{2+} and Pt^{2+} much larger than those previously reported, even larger than those of the commercial sorbents used to recover these metals. Moreover, this aspect is interesting since the complexation of the metal ions clearly modifies the electronic behavior of the nanotubes, opening a path to tune the electronic behavior of the tubes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The financial support of the MINECO (projects MAT2014-60104-C2-1-R and MAT2014-60104-C2-2-R), FEDER program, Autonomous Regional Government (J. de Andalucía, group RNM342) and Programa de Fortalecimiento de la I+D+i from UGR is acknowledged. The technical assistance of Centre of Instrumental Facilities, STI, of the University of Jaén is also acknowledged.

References

1 A. Wang, J. Song, D. Jia, W. Yu, L. Long, Y. Song, M. P. Cifuentes, M. G. Humphrey, L. Zhang, J. Shao and C. Zhang, *Inorg. Chem. Front.*, 2016, **3**, 296–305.
2 U. N. Maiti, W. J. Lee, J. M. Lee, Y. Oh, J. Y. Kim, J. E. Kim, J. Shim, T. H. Han and S. O. Kim, *Adv. Mater.*, 2014, **26**, 40–67.
3 A. Hirsch and O. Vostrowsky, in *Functional Molecular Nanostructures*, ed. A. D. Schluter, 2005, vol. 245, pp. 193–237.

4 A. Hirsch, *Angew. Chem., Int. Ed.*, 2002, **41**, 1853–1859.
5 X. H. Peng and S. S. Wong, *Adv. Mater.*, 2009, **21**, 625–642.
6 K. Balasubramanian and M. Burghard, *Small*, 2005, **1**, 180–192.
7 M. Shim, N. W. S. Kam, R. J. Chen, Y. Li and H. Dai, *Nano Lett.*, 2002, **2**, 285–288.
8 C. A. Dyke and J. M. Tour, *J. Phys. Chem. A*, 2004, **108**, 11151–11159.
9 S. Sakthinathan, T. Kokulnathan, S.-M. Chen, R. Karthik and T.-W. Chiu, *Inorg. Chem. Front.*, 2018, **5**, 490–500.
10 H. Yang, H. Zou, M. Chen, S. Li, J. Jin and J. Ma, *Inorg. Chem. Front.*, 2017, **4**, 1881–1887.
11 N. Karousis, N. Tagmatarchis and D. Tasis, *Chem. Rev.*, 2010, **110**, 5366–5397.
12 R. Barthos, D. Méhn, A. Demortier, N. Pierard, Y. Morciaux, G. Demortier, A. Fonseca and J. B. Nagy, *Carbon*, 2005, **43**, 321–325.
13 Y. Takeuchi, K. Fujiki and N. Tsubokawa, *Polym. Bull.*, 1998, **41**, 85–90.
14 F. Morales-Lara, M. Domingo-García, R. López-Garzón, M. Luz Godino-Salido, A. Peñas-Sanjuán, F. J. López-Garzón, M. Pérez-Mendoza and M. Melguizo, *Sci. Technol. Adv. Mater.*, 2016, **17**, 541–553.
15 X. Cai, M. Lin, S. Tan, W. Mai, Y. Zhang, Z. Liang, Z. Lin and X. Zhang, *Carbon*, 2012, **50**, 3407–3415.
16 A. Peñas-Sanjuán, R. López-Garzón, J. López-Garzón, M. Pérez-Mendoza and M. Melguizo, *Carbon*, 2012, **50**, 2350–2352.
17 B. L. Rivas and K. E. Geckeler, *Adv. Polym. Sci.*, 1992, **102**, 171–188.
18 E. P. Dillon, C. A. Crouse and A. R. Barron, *ACS Nano*, 2008, **2**, 156–164.
19 J. Zhou, C. Wang, Z. Qian, C. Chen, J. Ma, G. Du, J. Chen and H. Feng, *J. Mater. Chem.*, 2012, **22**, 11912.
20 V. K. Abdelkader-Fernández, M. Melguizo, C. García-Gallarín, M. D. López de la Torre, M. D. Gutiérrez-Valero, A. Martínez-Alonso, M. Domingo-García, F. J. López-Garzón and M. Pérez-Mendoza, *Catal. Sci. Technol.*, 2017, **7**, 3361–3374.
21 S. W. Won, J. Park, J. Mao and Y. S. Yun, *Bioresour. Technol.*, 2011, **102**, 3888–3893.
22 C. J. Liu, Y. Zhao, Y. Li, D. S. Zhang, Z. Chang and X. H. Bu, *ACS Sustainable Chem. Eng.*, 2014, **2**, 3–13.
23 E. P. Dillon, E. Andreoli, L. Cullum and A. R. Barron, *J. Exp. Nanosci.*, 2015, **10**, 746–768.
24 M. L. Godino-Salido, R. López-Garzón, P. Arranz-Mascarós, M. Dolores Gutiérrez-Valero, A. Santiago-Medina and J. García-Martín, *Polyhedron*, 2009, **28**, 3781–3787.
25 A. Martell and R. Smith, *Natl. Inst. Stand. Technol.*, 2004, 123–145.
26 C. Bazzicalupi, A. Bianchi, C. Giorgi, P. Gratteri, P. Mariani and B. Valtancoli, *Inorg. Chem.*, 2013, **52**, 2125–2137.
27 M. Savastano, C. Bazzicalupi, C. Giorgi, P. Gratteri and A. Bianchi, *Molecules*, 2017, **22**, 816.
28 J. E. Huheey, E. A. Keiter, R. L. Keiter and O. K. Medhi, *Inorganic Chemistry: Principles of Structure and Reactivity*, Pearson Education, 2006.

