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Carbon nanotubes functionalized with copper hexacyanoferrate nanoparticles for a selective extraction of cesium from liquid waste

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Abstract : Single-walled carbon nanotubes are functionalized with copper hexacyanoferrate nanoparticles for the liquid-solid extraction of cesium from liquid waste and contaminated water. The functionalization process is followed mainly by x-ray photoemission spectroscopy. Indeed, determining the chemical environment around carbon or nitrogen atoms allows to evidence the formation of covalent bonding. In addition, the signatures of iron and copper ions give information on the effective growth of hexacyanoferrate nanoparticles. Furthermore, the cesium sorption mechanism is investigated by comparing the peak intensities associated to the response of potassium and cesium ions. Finally, based on the liquid chromatography analyzes, the sorption of cesium with the functionalized carbon supports is studied. The main results of this work are the demonstration of both a good selectivity of cesium trapping and a high sorption capacity by hybrid single-walled carbon nanotubes.

Keywords : LIQUID WASTE, NANOTUBES, HEXACYANOFERRATE, FUNCTIONALIZATION, CESIUM TRAPPING

Introduction

Decontamination of radioactive water, whether from nuclear effluents from industry and research, or from nuclear accidents, is a major challenge to limit releases to the environment [1-2]. In particular, radioactive iodine (I-131) and cesium (Cs-137) are particularly toxic and found in large quantities in polluted waters [3-4]. It therefore becomes urgent to provide sustainable solutions for the treatment of contaminated water, in particular with radioactive cesium ions (Cs^+).

Several materials have been proposed for this application, but the frequent coexistence of other ions whose concentration is higher than Cs^+ limits the efficiency of decontamination. Thus, the use of selective sorbents is absolutely mandatory. Prussian blue analogues have been shown to be particularly relevant for this application. In particular, they are useful for the treatment of contaminated natural water or diluted wastes with typical Cs^+ concentrations ranging from 10^{-9} g L^{-1} for contaminated water and up to 10^{-4} g L^{-1} for low to intermediate level wastes [4]. However, once hydrated, this material forms sludge that is difficult to reprocess afterwards, which makes difficult its utilization [5-6]. Then, Prussian blue grafting tests on mesoporous silica have been carried out. This allows a continuous flowing on solid support, affording the treatment of large quantities of water. However this latter material exhibits a low sorption rate and has a weakness inherent in its chemical composition towards aggressive media such as basic medium [7-8].

Single walled-carbon nanotubes are solid materials displaying a high specific area, good mechanical and chemical resistances. However, pristine nanotubes (including multi-walled) exhibit a poor sorption capacity [9-10]. Outer surface functionalization with dimethyl-acetylene dicarboxylate increase significantly the whole sorption capacity but without any selectivity [11].

Consequently, in order to overcome all these drawbacks, this work is focused on the hexacyanoferrate nanoparticles (HCF, which are Prussian blue analogs) grafting onto single-walled carbon nanotubes (NT) in order to elaborate new hybrid system (HFC-NT) for a selective cesium extraction with high capacity.

Experimental section

Nanotubes are purchased from Carbon Solution, Inc.(reference P2-SWCNTs, of diameter $1.4 \pm 0,2\text{nm}$). Propargylamine (PRG) and Copper-hexacyanoferrate precursors are purchased from Sigma-Aldrich (99%) and used without further purification.

1- Functionalization with propargylamine

A mixture containing 60mg of NT with 25ml of pure PRG is prepared. The mixture is submitted to ultrasonication for 15

min following the procedure described elsewhere [10]. The mixture is then transferred into a teflon-lined steel autoclave and heated to 100°C during 24 hours. This blend is filtered and then washed with acetone in order to remove all PRG molecules in excess.

2- Cu-HFC-NPs growth

This step is based on two reactions, following the procedure described in a previous work [11]. The first step features the addition of a copper nitrate ($\text{Cu}(\text{NO}_3)_2$) solution in order to attach a Cu atom to the PRG. This Cu atom serves as a nucleation center for the further growth of the CuHCF-NP. The resulting system is carefully rinsed with acetone. The second step consists in the addition of a potassium ferrocyanide ($\text{K}_4\text{Fe}(\text{CN})_6$) solution aimed at initiating the growth of the first cell of the CuHCF-NP. Both solutions are prepared with a concentration of 10^{-2} M. This process is cycled three to four times.

4- Characterization

X-ray photoelectron spectroscopy (XPS) is performed on an ESCALAB 250 (Thermo Electron). The X-ray excitation is provided by a monochromatic Al K α (1486.6 eV) source. All XPS spectra are treated using the AVANTAGE software.

Liquid phase ionic chromatography (LPIC) is performed using an ICS-5000-Dionex instrument with 4 scans for each sample.

5- Cesium sorption

Cs^+ sorption measurements are carried out in batch mode on both pristine NT and on HCF-NT according to the following protocol: 10 mg of a buckypaper of carbon nanotubes are stirred with 20 mL of cesium nitrate solution using different concentrations (0.1 mM, 0.5 mM, 2 mM, 4 mM and 8 mM) for 24 h. Carbon nanotubes are recovered by filtration using filter paper with particle retention between 5 and 13 mm and thoroughly washed using Milli-Q water. The solid samples are then dried for further analyses, while the liquid phase is analyzed by LPIC.

Functionalization processes

The different functionalization steps are investigated by XPS. Figure 1 displays the low resolution spectra for pristine nanotube (black curve, 1), PRG grafted on NT (red curve, 2) and HCF-NT (blue curve, 3). For pristine NT, two chemical elements are identified: carbon atoms (peak around 285 eV) of the nanotubes and some oxygen (530 eV) probably covalently bond to the carbon network, giving rise to defects [12].

After PRG ($\text{H-C}\equiv\text{C-CH}_2\text{-NH}_2$) grafting, a new peak at around 400 eV is observed, featuring the presence of nitrogen [13]. After HCF nanoparticle growth $\text{K}_2\text{CuFe}(\text{CN})_6$, new and expected peaks assigned to potassium (295 eV), iron (730 eV) and copper (932 eV) appear in the photoemission spectrum (fig.1.c) [14,15]. To better investigate the functionalization process and the chemical bounding formed, high resolution measurements are required.

Figure 2 displays the deconvoluted C1s peak at each

functionalization step. Comparing the C1s peaks of pristine NTs (fig.2.a) with PRG grafted NT samples (fig.2.c), we clearly see changes around 286 eV (linked to CO or CN bonds [12]), especially in terms of full width at half maximum (FWHM) (1eV for pristine NT and 1.3 eV for PRG-NT).

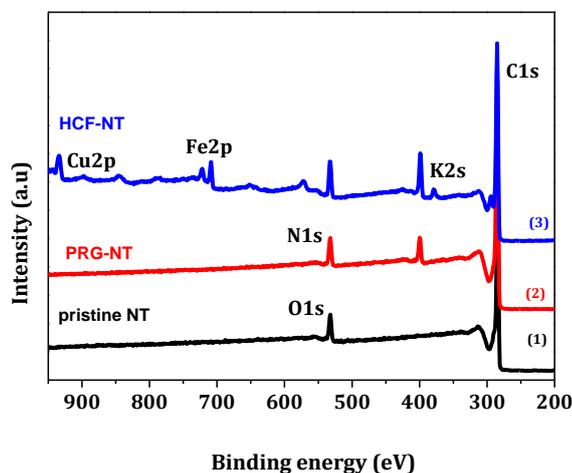


Figure 1: XPS survey at each grafting step

Quantitatively, this contribution has significantly increased (from 4% up to ~ 14%). This evolution is concomitant with a decrease of the sp² peak at 284.4 eV and an increase of the sp³ contribution at 285 eV. Indeed, NT functionalization with PRG leads to a change of sp² orbitals into sp³ orbitals in order to ensure a covalent bonding between the carbon atoms of the NT and PRG. In addition, the C-N bondings of the PRG molecules increase significantly the peak intensity at around 286 eV which can arise either from C-O or C-N (and even triple bonding between carbon atoms) [12]. For NT functionalized with HCF (Fig. 2.c), the signal around 286 eV (relative to C-N, C-O or C≡C bonds) decreases with respect to the PRG-NT (from ~ 14% to 10.6%). One possible assumption is to consider that the washing step after HCF functionalization- that is to say after the growth of hexacyanoferrate nanoparticles, PRG-CuHCF particles not covalently bound to NT could have been removed, which induces a decreasing of C≡C bond signal.

Typical binding energy for nitrogen atoms in cyanide groups of hexacyanoferrate molecules is between 397.5 eV and 400 eV [15]. Figure 3 shows the high resolution N1s spectra of PRG-NT (fig. 3.a) and HCF-NT (fig. 3.b) samples. The most important signal at around 399 eV is due to C-N bonding from the PRG molecules whereas the peaks at around 400 eV and 402 eV, assigned to N-C=O and nitrogen ions correspond to defects and contamination after the different chemical treatments. Following the growth of HCF nanoparticles, a new peak appears around 397.6 eV, assigned to the C≡N bonds expected in HCF nanoparticles [15].

Figures 4 and 5 display peaks at 708.3 and 932.7 eV

corresponding to Fe2p and Cu2p binding energies [14-15]. The Fe2p energy is in good agreement with the formation of Fe²⁺, as expected in case of copper HCF. Biesinger et al [14] analyzed different types of copper samples such as Cu and Cu₂O, and found the same Cu2p decomposition profile as in our sample.

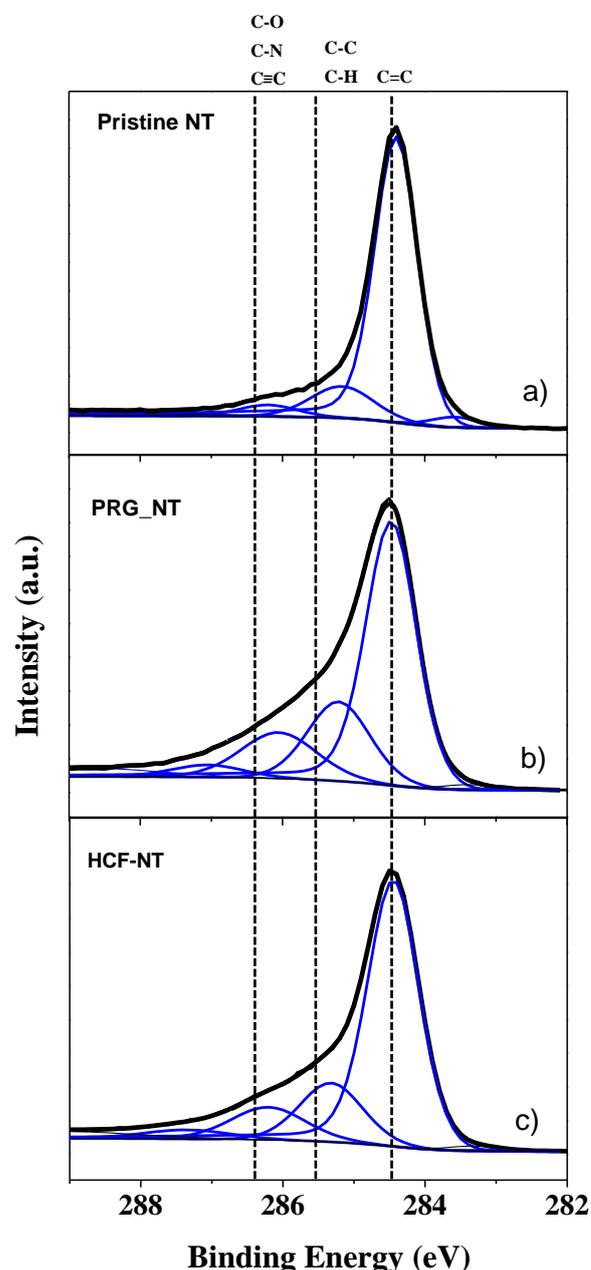


Figure 2: High resolution C1s x-ray photoemission spectra after each grafting step

They attributed the lower energy bond to Cu⁺ and the higher to Cu²⁺. In these compounds, Cu²⁺ is generally expected [15-16], but a reversible reduction reaction in Cu⁺ is sometimes reported [17]. It is worth mentioning that the intensity ration between

the two peaks depend on the area investigated.

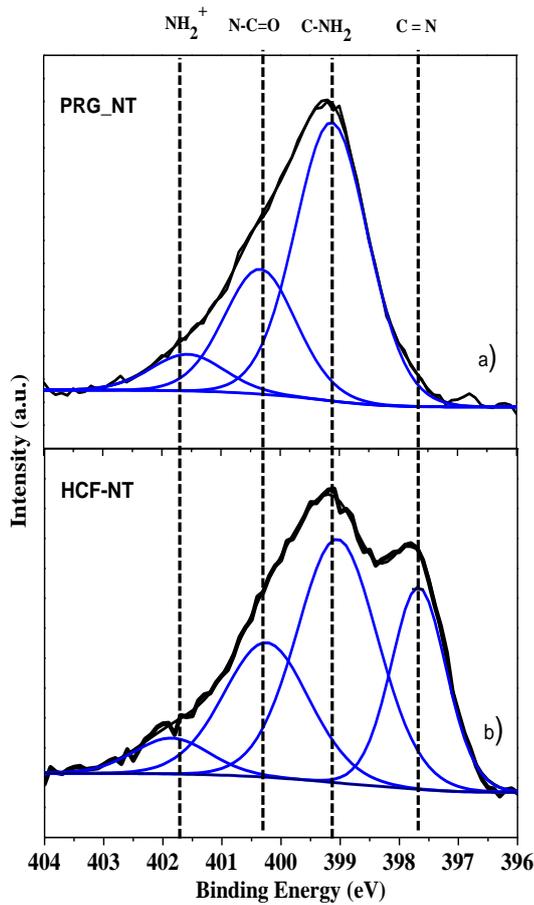


Figure 3: High resolution N1s x-ray photoemission spectra after each grafting step

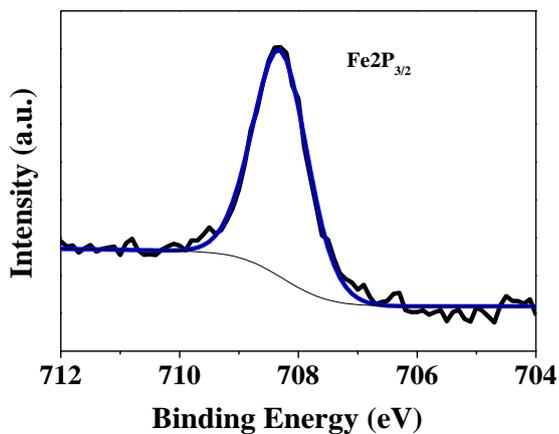


Figure 4: High resolution Fe2p x-ray photoemission spectrum of HCF-NT

It should be noted that the ratio $\text{Cu}^+ / \text{Cu}^{2+}$ strongly depends on the zone studied in our samples. As we do not believe in the heterogeneity of our samples, we assume a reduction under X-rays, leading to a transformation from Cu^{2+} to Cu^+ . Anyway, all the results are consistent with an efficient process of functionalization.

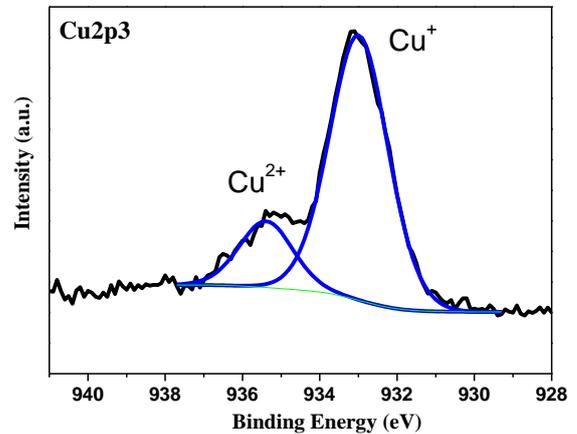


Figure 5: High resolution Cu2p x-ray photoemission spectrum of HCF-NT.

Cesium sorption capacity

The Cs^+ sorption measurements are carried out on both pristine and functionalized nanotubes with HFC.

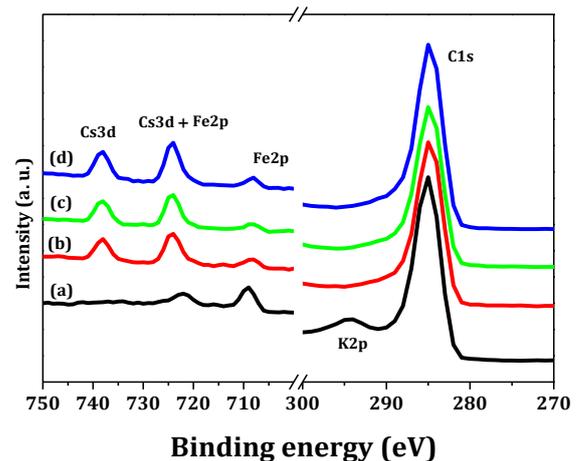


Figure 6: XPS survey for pristine HCF-NT (a) and exposed to solutions containing different Cs concentrations (b) 0.1 mM, (c) 2 mM, (d) 4mM

The XPS surveys of NT functionalized by HFC before and after exposure to CsNO_3 solutions of different Cs concentrations

(0.1mM, 2mM and 4mM) are presented in Figure 6. The presence of Cs is detected in two positions of binding energy: ~ 738 eV and ~ 724 eV [18] (Fig. b, c and d). The intensity of these peaks increases with the concentration of CsNO_3 . Concomitantly, the disappearance of the signal from potassium is observed. This result confirms an exchange between Cs^+ and K^+ ions within the HFC cubic structure. Finally, we observe Cs^+ XPS signal that increases very slowly, suggesting that sites available for Cs^+ sorption are rapidly saturated.

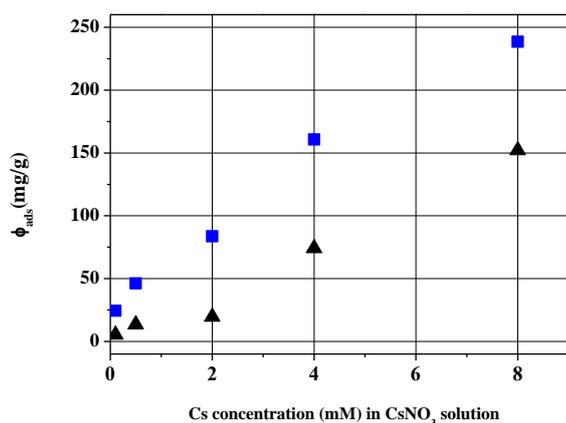


Figure 7: Sorption isotherm of Cs^+ on NT and HCF-NT

In order to go further in understanding the sorption mechanism, we also conducted LPIC analyzes of the cesium solution before and after exposure to HCF-NT. The Cs^+

sorption isotherm by pristine and functionalized nanotubes with HFC are shown in figure 7. Both NT materials show increasing sorption capacity with increasing concentration of Cs^+ , although it is still lower for pristine NT with respect to HCF-NT (150 mg.g^{-1} and 230 mg.g^{-1} respectively). One way to evaluate the proportion of Cs^+ ions complexed in HFC nanoparticles (i.e. selectively trapped) is to subtract the sorption isotherm from the pristine NT to that of HFC. Thus, for Cs concentration of 4mM, the selective sorption of Cs reaches a value of about 80 mg.g^{-1} (about a third of the total sorption of the HCF-NT). This value compares rather well with other materials generally used for Cs extraction.

Conclusions

Hexacyanoferrate nanoparticles (prussian blue analogs) have been successfully grafted at the outer surface of carbon nanotubes using propargylamine molecules as intermediate species. The different steps of the whole functionalization process have been investigated mainly by means of x-ray photoemission spectroscopy. The study of the different chemical environments around the carbon and nitrogen atoms allowed to evidence the formation of the expected covalent bondings at each step of the process. The nature of iron and copper ionic species confirms the growth of copper hexacyanoferrate nanoparticles. Cesium sorption capacity has been studied by liquid phase ionic chromatography. The reached value of 80 mg/g is particularly encouraging. Finally, ion exchange mechanism between potassium and cesium species has been confirmed by photoemission measurements.

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