Electrochemical functionalization at anodic conditions of multi-walled carbon nanotubes with chlorodiphenylphosphine

Andrés Felipe Quintero-Jaime [a], Alessio Ghisolfi [b], Diego Cazorla-Amorós [b], Emilia Morallón [a],*

[a] Departamento de Química Física and Instituto Universitario de Materiales de Alicante (IUMA), University of Alicante, Ap. 99, 03080, Alicante, Spain
[b] Departamento de Química Inorgánica and Instituto Universitario de Materiales de Alicante (IUMA), University of Alicante, Ap. 99, 03080, Alicante, Spain

GRAPHICAL ABSTRACT
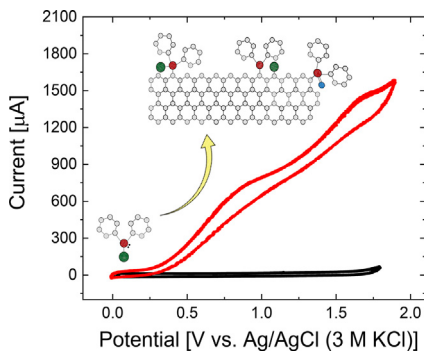
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ABSTRACT

Covalent functionalization of multi-walled carbon nanotubes (MWCNTs) and oxidized MWCNTs (o-MWCNTs) with chlorodiphenylphosphine (Ph_2PCl) has been studied by cyclic voltammetry in organic medium. Depending the upper potential limit used in the electrochemical functionalization, different amount of phosphorus incorporation n is obtained, as result of the formation of radical species during the electrochemical oxidation of the Ph_2PCl. The electrochemical oxidation of Ph_2PCl promotes the covalent attachment of diphenylphosphine-like structure on the carbon nanotube surface. At the same time, the incorporation of Cl on the carbon nanotubes is observed during the functionalization. Furthermore, the presence of oxygen surface groups on the MWCNTs provides a favorable attachment of the Ph_2P^+ species, which has promoted preferentially the formation of C—P bonds, whereas the amount of Cl is reduced.

1. Introduction

Mechanical and electronic properties of carbon nanotubes (CNTs) have stimulated their use in catalysis, adsorption and sensing applications [1-3]. In this sense, surface properties play a triggering role in the material performance, due to the great importance of the interfacial interactions between the CNTs and the medium [4,5]. Therefore, new trends on CNTs surface modification (both non-covalent and covalent) are nowadays being developed not only for improving the dispersibility of the CNTs, but also for the enhancement of their functionality through the incorporation of different functional groups [5,6].

A high diversity of molecules have been used for CNTs functionalization using different routes, including chemical and electrochemical methods [7]. Under oxidative conditions, incorporation

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* Corresponding author.
    E-mail address: morallon@ua.es (E. Morallón).

of surface oxygen groups have been used to improve the dispersibility of CNTs in polar media [3,7]. Furthermore, grafting of aromatic amines with different substituents such as phosphonic groups, sulphonic and carboxylic moieties by electrochemical oxidation in aqueous medium, has also proved to promote the incorporation of different heteroatoms and functionalities in the CNTs [8-11], providing suitable platforms for electrode materials for energy storage applications and electrocatalytic reactions such as oxygen reduction reaction (ORR) [10,11]. In addition, phosphorus surface groups incorporated in carbon materials are gradually transformed from less-to more-oxidized highly stable species. Then the electro-oxidation inhibition induced by phosphorus functionalities entails a general strategy to increase the electrochemical stability of carbon materials [12].

Interestingly, until now, the use of organophosphorus compounds such as phosphine derivatives and an organic solvent has been only partially explored for the functionalization of CNTs, despite the important role that these species have in many organic reactions, complexations with metal centers and related catalytic reactions [13,14] which make them potentially ideal candidates for the preparation of novel catalysts based on CNTs [5,15]. In particular, previous works reported the incorporation of phosphines by different chemical routes employing solvent-free reactions in a molten blend of single walled carbon nanotubes (SWNCTs) with tertiary phosphines [16] or by coupling reactions through arylation reactions or using carboxylic moieties, which in some cases are thermally treated, generating surface and P-containing CNTs [13,17]. Among these achievements the lack of results applying electrochemical methods in organic solvent suggests that those procedures have not been explored yet.

Electrochemical functionalization procedures are based on the formation of highly reactive species under oxidative or reductive conditions, which results in the formation of a covalent bond with the electrode [7,18]. Typical examples of electrochemical functionalization are in reduction conditions of diazonium salts [19,20]. In those cases, radical species present high preference to attack the surface, specially carbon electrodes by generating the covalent bond [7].

Concerning the electrochemistry of organophosphorus compounds, several authors have shown that under reductive conditions, the phosphorus atom in the phosphine (triphenylphosphine, triphenylphosphine oxide and chlorodiphenylphosphine) is directly involved in the electron-transfer and affords the formation of an anionic radical phosphine [21-23]. Interestingly, phosphine radical species can display nucleophilic or electrophilic behavior, depending on the conditions (reductive or oxidative) and this makes them susceptible to react with a wide range of substrates [23-25].

In this work, Multi-Walled Carbon Nanotubes (MWCNTs) have been electrochemically functionalized during electrochemical oxidation of chlorodiphenylphosphine (Ph$_2$PCl) using cyclic voltammetry at different upper potential limits in organic medium. The results suggest that the formation of radical species, which react with the MWCNTs surface, generates Ph$_2$P-CNTs bonds. Moreover, the incorporation of P heteroatom also results in the incorporation of chlorine in the surface of MWCNTs. The amount of phosphorus and chlorine incorporated was followed by XPS and showed a potential dependence. Diphenylphosphine species covalently bonded to the MWCNTs affect the electrochemical response of the MWCNTs in aqueous acid medium and the electron transfer of a conventional redox probe (Fe[(CN)$_6$]$^{3-/4-}$). Furthermore, the presence of oxygen functional groups in the MWCNT promotes a secondary phosphine anchoring route, which increase even more the P doping by the formation of phosphonate and phosphinate groups.

2. Experimental section

2.1. Reagents and equipment

Multi-Walled Carbon Nanotubes with purity 95% (8 nm of diameter) and 10–30 μm length were purchased from Cheap Tubes Inc. (Cambridgeport, USA). N,N-Dimethylformamide, extra pure, provided by Scharlau, was used as received and employed to disperse the MWCNTs. Nitric acid (65%) was purchased from Panreac.

Sulphuric acid (H$_2$SO$_4$-98%) and acetonitrile (MeCN-0.001% in H$_2$O) analytical reagent for the preparation of electrolytes, were obtained from VWR Chemicals. Chlorodiphenylphosphine (Ph$_2$PCl, ≥ 96%) and tetrabutylammonium hexafluorophosphate (TBA, ≥ 98%) were purchased from Sigma-Aldrich. Potassium dihydrogen phosphate (KH$_2$PO$_4$) and Dipotassium hydrogen phosphate (K$_2$HPO$_4$) were obtained from Merck and VWR Chemicals, respectively. Both reagents were used to prepare phosphate buffer solutions (0.1 M PBS, pH = 7.2). Potassium hexacyanoferrate (II) trihydrate and potassium hexacyanoferrate (III) as redox probe were obtained by Sigma-Aldrich. All the aqueous solutions were prepared using ultrapure water (18 MΩ cm, Purelab Ultra Elga equipment). The gases N$_2$ (99.999%) and H$_2$ (99.999%) were provided by Air Liquide.

2.2. Electrochemical modification of MWCNTs with chlorodiphenylphosphine

2.2.1. Chemical functionalization of Multi-Walled carbon nanotubes
MWCNTs were oxidized by a treatment in a nitric acid solution. In particular, 200 mg of pristine MWCNTs were dispersed in 100 mL of 3 M HNO$_3$ at 120 °C for 24 h, under reflux. Oxidized MWCNTs (o-MWCNTs) were filtered and washed with ultrapure water until the solution was neutralized. The filtered solid was then dried in vacuum at 60 °C for 24 h. This process not only removes the metal impurities in the CNTs, but also produces surface oxygen groups that facilitates the dispersibility in water; hence, using sonication bath for 10 min, a dispersion of 1 mg mL^{-1} of o-MWCNT was obtained. Table 1 reports the amounts of CO and CO$_2$ desorbed, as well as the total oxygen amount (calculated as CO + 2CO$_2$), obtained from the TPD experiments for pristine and oxidized MWCNTs samples [26]. Table 1 also includes the BET surface area of the materials.

2.2.1.1. Electrode preparation. Working electrode was prepared using dispersions of 1 mg mL^{-1} in DMF or water for MWCNTs and o-MWCNT, respectively. 5 μL of the dispersion was deposited onto a glassy carbon (GC) surface, previously sanded with emery paper and polished using 1 and 0.05 μm alumina slurries. This procedure was repeated twice to obtain a loading of 10 μg of carbon material on the GC electrode.

2.2.1.2. Electrochemical modification of carbon nanotubes. Modification of the carbon nanotubes was performed using an EG&G Princeton Applied Research Model 263A Potentiostat/Galvanostat using a standard three-electrode cell configuration, in which the glassy carbon electrodes modified with MWCNTs or o-MWCNTs were the working electrode (WE), a graphite rod was used as counter electrode (CE) and Ag/AgCl/Cl$^-$ (3 M KCl) was the reference electrode. This latter was introduced in the electrolyte in absence of the Ph$_2$PCl using a Luggin capillary. Electrochemical modification was carried out in organic electrolyte (CH$_3$CN + 0.1 M TBA) in presence of 0.1 M PPh$_2$Cl previously deoxygenated by bubbling nitrogen. The modification of MWCNTs and o-MWCNTs was performed by cyclic voltammetry submitting the samples at different upper potential limits maintaining constant the lower potential

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Table 1
Porous texture and surface chemistry characterization for both MWCNTs samples.

Sample	S_{BET} / $m^2\ g^{-1}$	CO_2 / $\mu mol\ g^{-1}$	CO / $\mu mol\ g^{-1}$	Total O / $\mu mol\ g^{-1}$
MWCNT	208	120	600	840
o-MWCNT	460	2477	3502	8456

limit. Electrodes were cycled for 30 min at 50 mV s^{-1}. After electrochemical treatment, CNTs electrodes were washed with an excess of acetonitrile and acetone to remove eventual remaining electrolyte and adsorbed products. The modified samples were named as MWCNT-X, o-MWCNT-X and MWCNT-Ph$_2$PCl-X, o-MWCNT-Ph$_2$PCl-X for those synthesized in absence and presence of the Ph$_2$-PCl, respectively. X corresponds to the upper potential limit employed.

2.3. Electrochemical characterization

Electrochemical behavior of the synthesized carbon materials was evaluated by cyclic voltammetry in different electrolytes (organic media – MeCN + 0.1 M TBA and 0.5 M H$_2$SO$_4$ aqueous solution), employing the standard three electrode configuration cell, where the glassy carbon modified with CNTs was the working electrode (WE), platinum wire was the counter electrode (CE) and a reversible hydrogen electrode (RHE) in case of the aqueous solution or a Ag/AgCl (3 M KCl) electrode for the organic medium, introduced in the same electrolyte, were used as reference electrode (RE), respectively. Potential range between was fixed 0 to 1 V vs. RHE at 50 mV s^{-1}. Additionally, electron-transfer efficiency was evaluated by cyclic voltammetry in a 0.1 M PBS (pH = 7.2) + 10 mM Fe[(CN)$_6$]$^{3-/4}$ in the same electrochemical cell set-up described above.

2.4. Physicochemical characterization

X-Ray photoelectron spectroscopy (XPS) was performed in a VG-Microtech Mutilab 3000 spectrometer and Al Kα radiation (1253.6 eV). The deconvolution of the XPS C1s, O1s, P2p and Cl2p was done by least squares fitting using Gaussian-Lorentzian curves, while a Shirley line was used for the background determination. The Cl2p spectra have been analyzed considering the spin–orbit splitting into Cl2p3/2 and Cl2p1/2 with a 2:1 peak area ratio and 1.6 eV splitting. Analysis of P2p spectra has been performed considering the spin–orbit splitting into P2p3/2 and P2p1/2 with a 2:1 peak area ratio and 0.87 eV splitting.

3. Results and discussion

3.1. Electrochemical functionalization of MWCNTs in organic medium with Ph$_2$PCl

Fig. 1 shows the cyclic voltammograms in which the upper potential limit was changed from 0.7 to 2.0 V in organic electrolyte, to understand the electrochemical behavior in absence (A) and presence (B) of the Ph$_2$PCl, respectively.
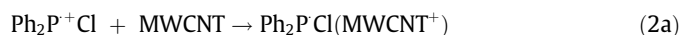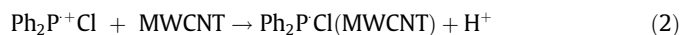
In absence of Ph$_2$PCl (Fig. 1-A), MWCNTs present a quasi-rectangular voltammogram between 0 and 0.6 V with the absence of redox processes as corresponds to a double-layer capacitive behavior. The increase in the upper potential limit results in the appearance of redox processes as consequence of the oxidation of the MWCNTs surface at potentials higher than 0.7. Moreover, at higher upper potential limits, oxidation currents are clearly observed.

In presence of Ph$_2$PCl (Fig. 1-B), an oxidation current with an on-set potential at around 0.45 V can be observed. The intensity

of this oxidation current increases with the upper potential limit and it can be associated with the oxidation of Ph$_2$PCl. Two oxidation processes at higher potentials (processes A1 and A2 in Fig. 1-B) are observed which do not have the corresponding reduction processes during the reverse scan. Electrochemistry of triphenylphosphine on vitreous carbon electrodes in acetonitrile has been studied in detail [25]. It has been observed that the oxidation of triphenylphosphine shows an oxidation peak corresponding to the formation of a radical cation which can react with the residual water or other nucleophiles to produce triphenylphosphine oxide or the corresponding derivative [25]. Then, according to this, the oxidation of Ph$_2$PCl, that produces the A1 oxidation process at similar potentials as with triphenylphosphine, could be associated to the formation of a radical cation:

$$Ph_2PCl \rightarrow Ph_2P^+Cl + e^- \qquad (1)$$

This radical cation may react with the MWCNTs (that participates as a nucleophile) according with Eq. (2) (or Eq. (2a) considering that the positive charge may be stabilized in the MWCNT), which is similar as that proposed for triphenylphosphine and is a fast irreversible reaction, followed by a charge transfer reaction (Eq. (3)) [25]:

$$Ph_2P^+Cl \ + \ MWCNT \rightarrow Ph_2P^\cdot Cl(MWCNT) + H^+ \qquad (2)$$

$$Ph_2P^+Cl \ + \ MWCNT \rightarrow Ph_2P^\cdot Cl(MWCNT^+) \qquad (2a)$$

$$Ph_2P^\cdot Cl(MWCNT) \rightarrow Ph_2PCl(MWCNT) + e^- \qquad (3)$$

Since the C—Cl and P—Cl bonds energy are similar, it is possible that Cl atom may react with the MWCNT according with the following reactions (Eq. (4)):

$$Ph_2P^\cdot Cl(MWCNT) \leftrightarrow Ph_2PCl(MWCNT^\cdot)$$
$$\leftrightarrow Ph_2P^\cdot (MWCNT - Cl) \qquad (4)$$

Further charge transfer reaction like that indicatd in Eq.3 may occur producing Ph$_2$P and Cl containing MWCNT: Ph$_2$P(MWCNT – Cl).

In presence of residual water or oxygen functional groups, Ph$_2$P$^\cdot$Cl(MWCNT) species can be transformed into the corresponding phosphine oxide through the following reaction (Eq. (5)) (written in this case for water):

$$Ph_2P^\cdot Cl(MWCNT) + \ H_2O \leftrightarrow Ph_2(MWCNT)P$$
$$= O^\cdot + HCl + \ H^+ + e^- \qquad (5)$$
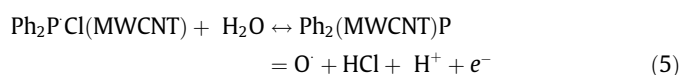
It must be noted that the reactions with MWCNT may occur through the C atoms at the MWCNT walls or through oxygen functional groups.

Based on the electrochemical stepwise potential study, different upper potential limits were selected, employing different electrode samples for each potential, in order to investigate the functionalization of the MWCNTs during the oxidation of the organophosphorus compound.

Fig. 2 shows the voltammograms obtained for the electrodes in absence (black line) and in presence (red line) of the phosphine compound in the electrolyte. Cyclic voltammograms of the electrodes in absence of the Ph$_2$PCl showed that when the upper potential limit increases above 1.2 V, a reversible redox process
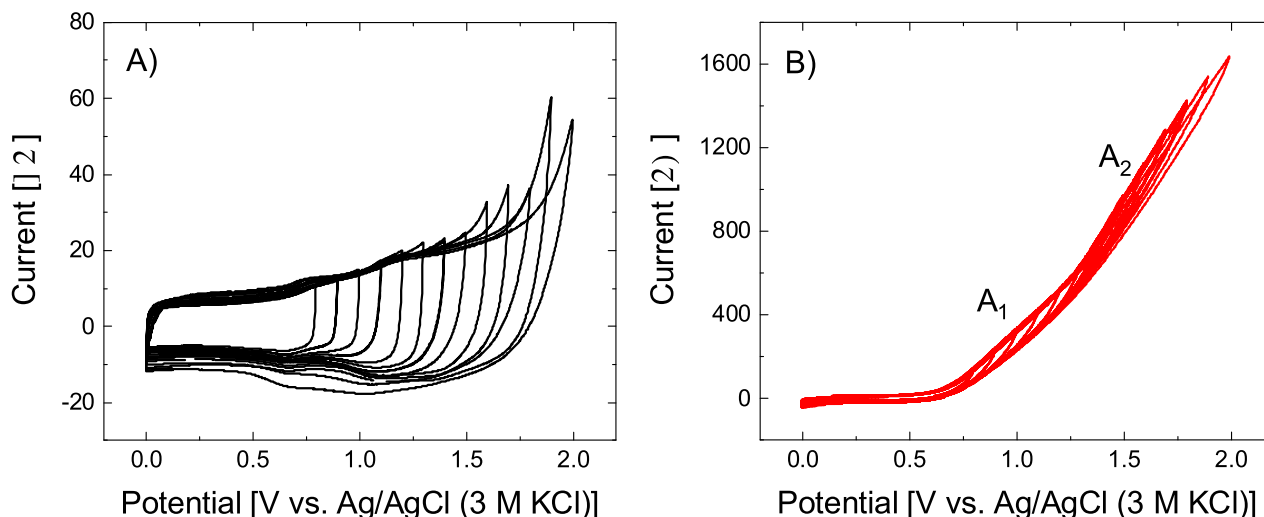
Fig. 1. Cyclic voltammograms at different upper potential limit for: A) MWCNTs in MeCN + 0.1 M TBA and B) MWCNTs in MeCN + 0.1 M TBA + 0.1 M Ph$_2$PCl at 50 mV s^{-1}.

at 0.7 V is observed, corresponding to possible surface species generated during the oxidation of the MWCNTs. However, the oxidation current is very low in comparison with the voltammograms in presence of Ph$_2$PCl.

The presence of chlorodiphenylphosphine in the solution produces a high oxidation current related with the oxidation of this compound at an on-set potential of 0.43 V and an oxidation current at around 1.03 V, leading to the formation of the radical cation. When the upper potential limit increases, the current associated with the oxidation of the phosphine raises considerably, thus further oxidation processes occur. These observations are in agreement with the equations previously presented.

Fig. 3 shows the electrochemical characterization of the electrodes synthesized in Fig. 2 in organic medium in absence of the Ph$_2$PCl. In all the electrodes, including the pristine MWCNTs, a redox process at around 0.65 V can be observed. Interestingly, when the upper potential limit increases for the materials that contain the phosphine compound, an important decrease in the voltammetric charge is observed which can be due to a loss of the accessible area on the MWCNTs. This can be associated with some steric hindrance induced by the phenyl groups in the phosphine. It should also be noted that the functionalized MWCNTs with these species do not show any additional redox processes thus showing their lack of electroactivity in this organic medium. In absence of Ph$_2$PCl a small increase of the double layer charge is observed when rising the upper potential limit (see Figure S1 in supporting information), which is in agreement with oxidation of the MWCNTs, as observed in aqueous and organic media. XPS characterization was also performed and results will be discussed further.

3.2. Electrochemical characterization of functionalized MWCNTs with chlorodiphenylphosphine in acidic aqueous solution.

Fig. 4 shows the electrochemical characterization of the electrodes synthesized at 1.2 V and 1.8 V. In acid medium (Fig. 4-A and B) the electrodes synthesized in presence of Ph$_2$PCl show lower values of voltammetric charge in comparison with the electrodes synthesized in absence of Ph$_2$PCl, as was observed in organic medium. This behavior can be explained considering the steric hindrance effects induced by the phenylphosphine moieties.

In order to evaluate the efficiency of the electron transfer of the modified MWCNTs, cyclic voltammetry has been performed in presence of Fe[(CN)$_6$]$^{3-/4-}$ redox couple (See Fig. 4-C and D). All

the cyclic voltammograms showed the redox couple associated with the one electron transfer process of iron. On one hand, electrodes synthesized in absence of Ph$_2$PCl (MWCNT-1.2 and MWCNT-1.8) present a peak potential separation from 113 to 323 mV, respectively. This behavior indicates that the increase in the oxidation potential, produces an increase in the irreversibility of the redox processes. From the peak potential separation, it can be estimated the standard electrochemical rate constant (k^0) according to the Nicholson method [27,28]. The values obtained are 2.9x10^{-5} and 1.7x10^{-6} m s^{-1} for MWCNT-1.2 and MWCNT-1.8 respectively. As previously reported, the redox couple behavior is affected by the presence and nature of the surface functionalities on the MWCNTs [29]. In this sense, the increase in the oxidation potential of the MWCNTs in organic medium induces defects in the carbon nanotubes, which produce a loss of the conjugated structure of the carbon materials by formation of some functionalities by electrooxidation.

On the other hand, the voltammograms obtained for MWCNTs-Ph$_2$PCl-1.2 and MWCNTs-Ph$_2$PCl-1.8 present a different behavior in comparison with the MWCNTs modified in absence of Ph$_2$PCl. The MWCNTs-Ph$_2$PCl-1.2 shows an increase in the peak potential separation (540 mV) indicating an increase in the irreversibility of the electron transfer (1.16x10^{-7} m s^{-1}); however, the MWCNTs-Ph$_2$PCl-1.8 shows an important decrease in the peak potential separation (160 mV) in comparison with the MWCNT-1.8 sample, which corresponds to an electrochemical rate constant of 1.3x10^{-5} m s^{-1}, showing an improvement in the reversibility of the electron transfer kinetics. This can imply that during the electrochemical oxidation of the Ph$_2$PCl at low upper potential limits the functionalities introduced in the MWCNTs produces a hindrance to the electron transfer; however, when the potential increases these functionalities can be removed by further oxidation, thus facilitating the electron transfer with values of peak potential separation close to the value obtained for pristine MWCNTs (see Figure S2 in supporting information).

3.3. XPS characterization of electrochemically functionalized MWCNTs in presence of Ph$_2$PCl

Fig. 5 shows the P2p spectra obtained by XPS analyses of the different electrochemically modified MWCNTs in presence of Ph$_2$PCl.

The P2p spectra for all modified MWCNTs contain a main peak at a binding energy of about 133.5 eV. It is important to indicate that for MWCNTs-Ph$_2$PCl-1.05, XPS analysis showed for P2p a sig-

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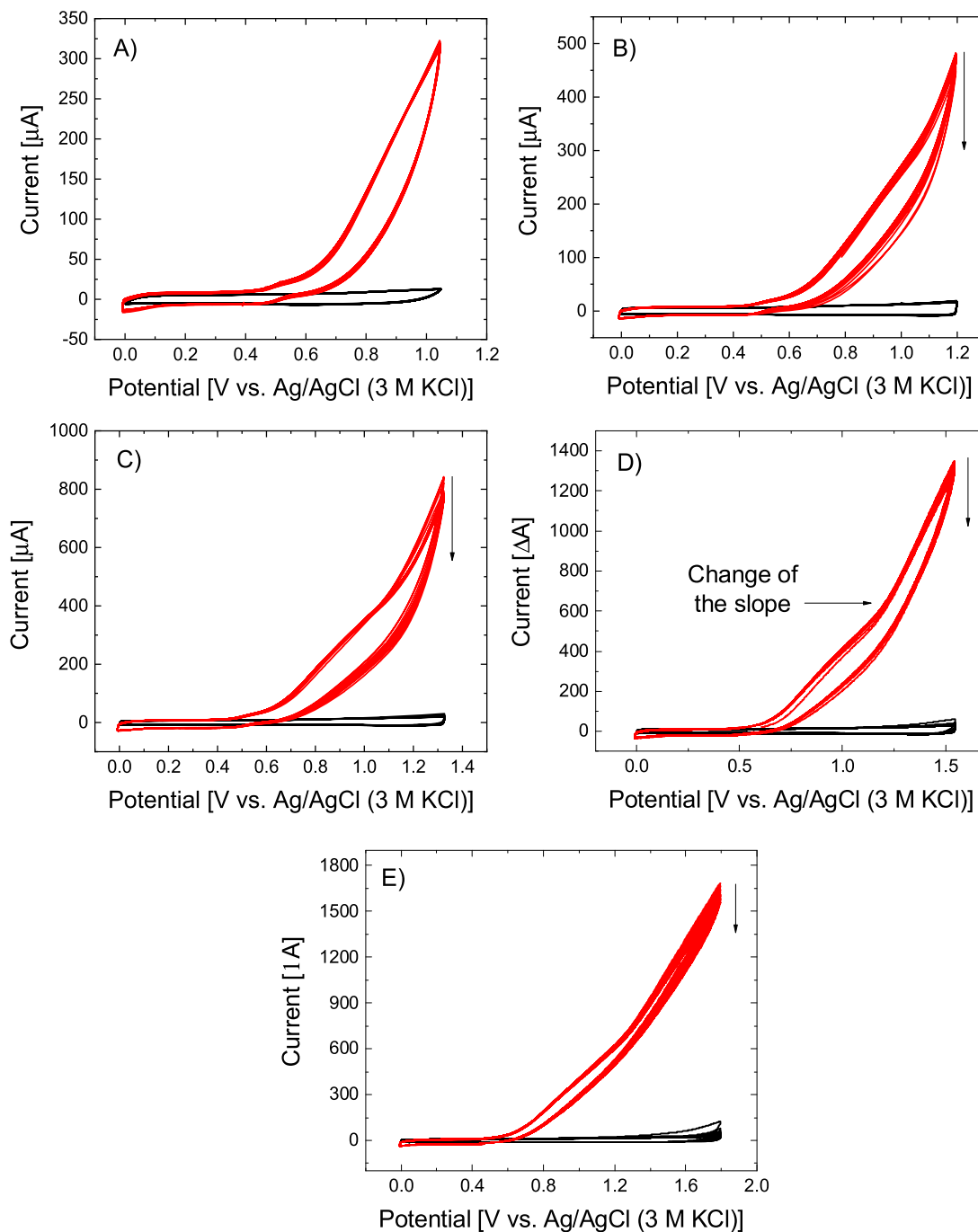Journal of Colloid and Interface Science 623 (2022) 915–926

Fig. 2. Cyclic voltammograms for the MWCNTs at different upper potential limits: A) 1.05, B) 1.2, C) 1.33, D) 1.55 and E) 1.8 V, in absence (black line) and presence (red line) of 0.1 M Ph₂PCl. Conditions: 0.1 M TBA in MeCN at 50 mV s⁻¹, under inert atmosphere for 30 min of cycling.

nal/noise ratio, close to the detection limit of the technique, and this prevented a proper characterization. The P2p broad peak can be deconvoluted in different doublets with an area ratio of 0.5 and a distance between peaks of 0.87 eV. Then, in all cases the presence of three different contributions is observed at binding energies of 132.7 ± 0.4 eV, 134.1 ± 0.2 eV and 135.7 ± 0.4 eV. The first doublet has been widely associated in literature to the P—C bond [8], particularly, the P—C energy binding in P-modified MWCNTs shows similar values of binding energy in triphenylphosphine reported previously [30]. The second doublet to about 134.1 eV are corresponding with the P—O species, such as P—O—C and P=O oxidized species [31]. Meanwhile, the contribution at the

highest binding energies might be related with the oxidized species generated by an overoxidation of the P—O/P=O bonds, generated during the electrochemical functionalization [32]. It is important to highlight that no phosphate groups coming from the electrolyte were present in the electrode after the modification (this species shows binding energy at around 138.1 to 139.5 eV [33], see Figure S3 in supporting information), hence the observed P doping is generated only by electrochemical oxidation.

As mentioned before, at the same time that phosphorus species are incorporated onto the MWCNTs surface, the formation of Cl—C bonds on surface may take place. This was confirmed by XPS. Fig. 6 shows the XPS spectra for Cl2p which can be deconvoluted in dou-
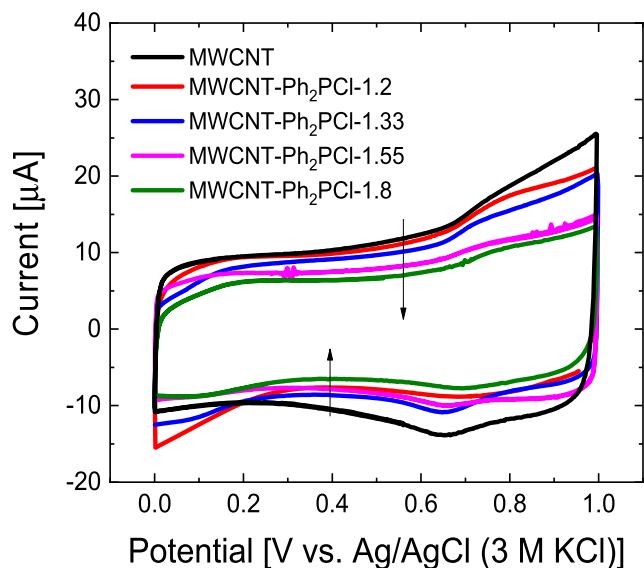
Fig. 3. Cyclic voltammograms of MWCNTs functionalized in presence of Ph$_2$PCl at different upper potential limits. Conditions: 0.1 M TBA in MeCN at 50 mV s^{-1}, under inert atmosphere.

blets with an area ratio of 0.5 and a distance between peaks of 1.6 eV. The incorporation of chlorine species on the MWCNTs surface could be related with the presence of organic chlorine (C—Cl)

peak with binding energy at around 200.8 ± 0.4 eV [34,35]. This contribution was the main species observed at upper potential limits lower than 1.33 V. Once upper potential limit was increased (1.55 and 1.8 V), a second contribution was observed at 198.4 ± 0. 4 eV, which can be related to the presence of chloride anions, that can be possibly formed during the oxidation of the Ph$_2$PCl. Interestingly, the presence of chloride anions, which increase with the upper potential limit implies that during the oxidation of the Ph$_2$-PCl, chlorine is released, what can be in agreement with Eq. (5).

The amounts of P and Cl on the electrochemically functionalized MWCNTs are compiled in Table 2. The results show that both species present a somewhat different incorporation depending on the upper potential limit. It must be noted that the reaction between the Ph$_2$PCl and the MWCNT in absence of potential, does not produce significant incorporation of P or Cl species. In fact, only P was detected with a 0.21 at% which is close to the detection limit.

The faradic efficiency of the electrochemical functionalization has been estimated from the voltametric charge in Fig. 2 and considering the suggested reactions occurring during the functionalization (equations 1–5), and the values have been compared with the theoretical charge obtained from the amount of P determined by XPS. It can be observed that faradic efficiencies are low and that, as expected, the efficiency decreases with the upper potential limit.

Phosphorus species in the electrochemically modified MWCNTs show a linear tendency with the increase of the upper potential limit (Fig. 7-A), which is in agreement with the increase in the current of the radical cation formation observed in the voltammograms (Fig. 2). Contribution of the different phosphorus species
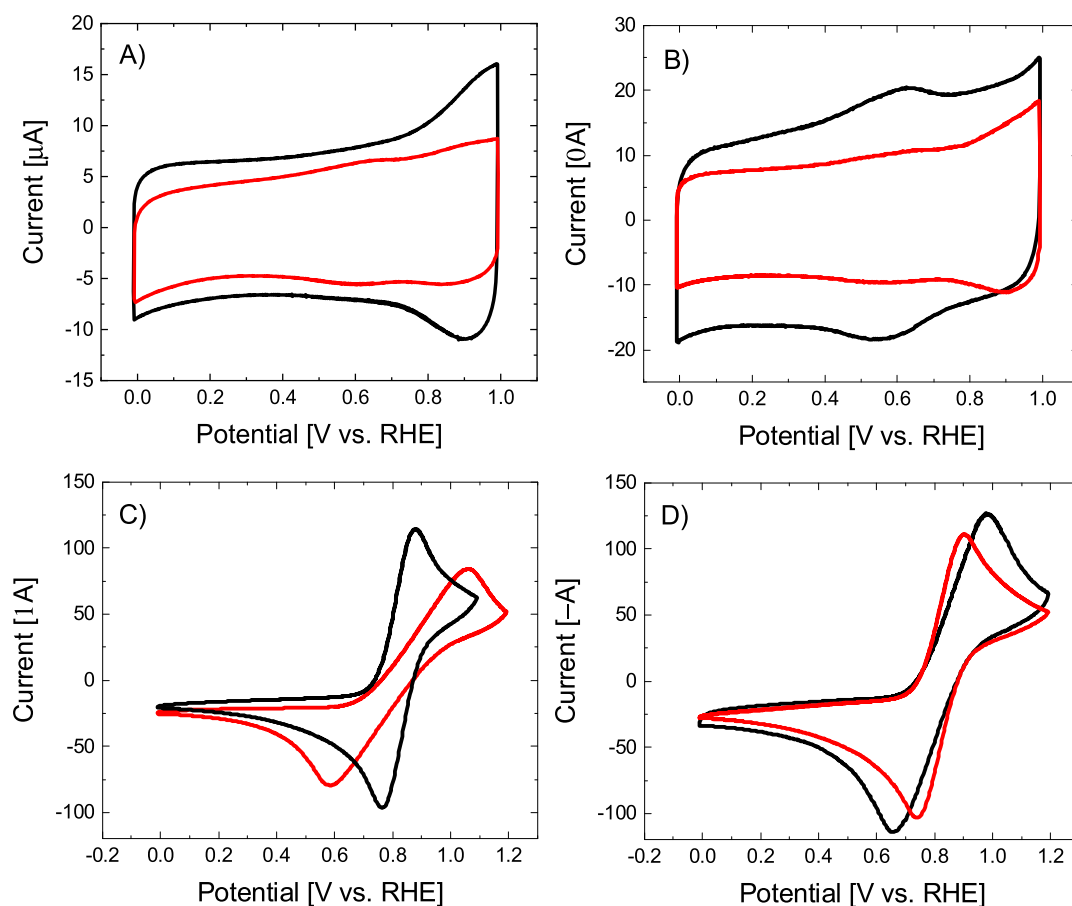

Fig. 4. Cyclic voltammograms in 0.5 M H$_2$SO$_4$ of A) MWCNT-1.2 (black line) and MWCNT-Ph$_2$PCl-1.2 (red line). B) MWCNT-1.8 (black line) and MWCNT-Ph$_2$PCl-1.8 (red line). Cyclic voltammograms in 0.1 M PBS (pH = 7.2) + 10 mM Fe[(CN)$_6$]$^{3-/4}$ of C) MWCNT-1.2 (black line) and MWCNT-Ph$_2$PCl-1.2 (red line). D) MWCNT-1.8 (black line) and MWCNT-Ph$_2$PCl-1.8 (red line). v$_{scan}$ 50 mV s^{-1}.
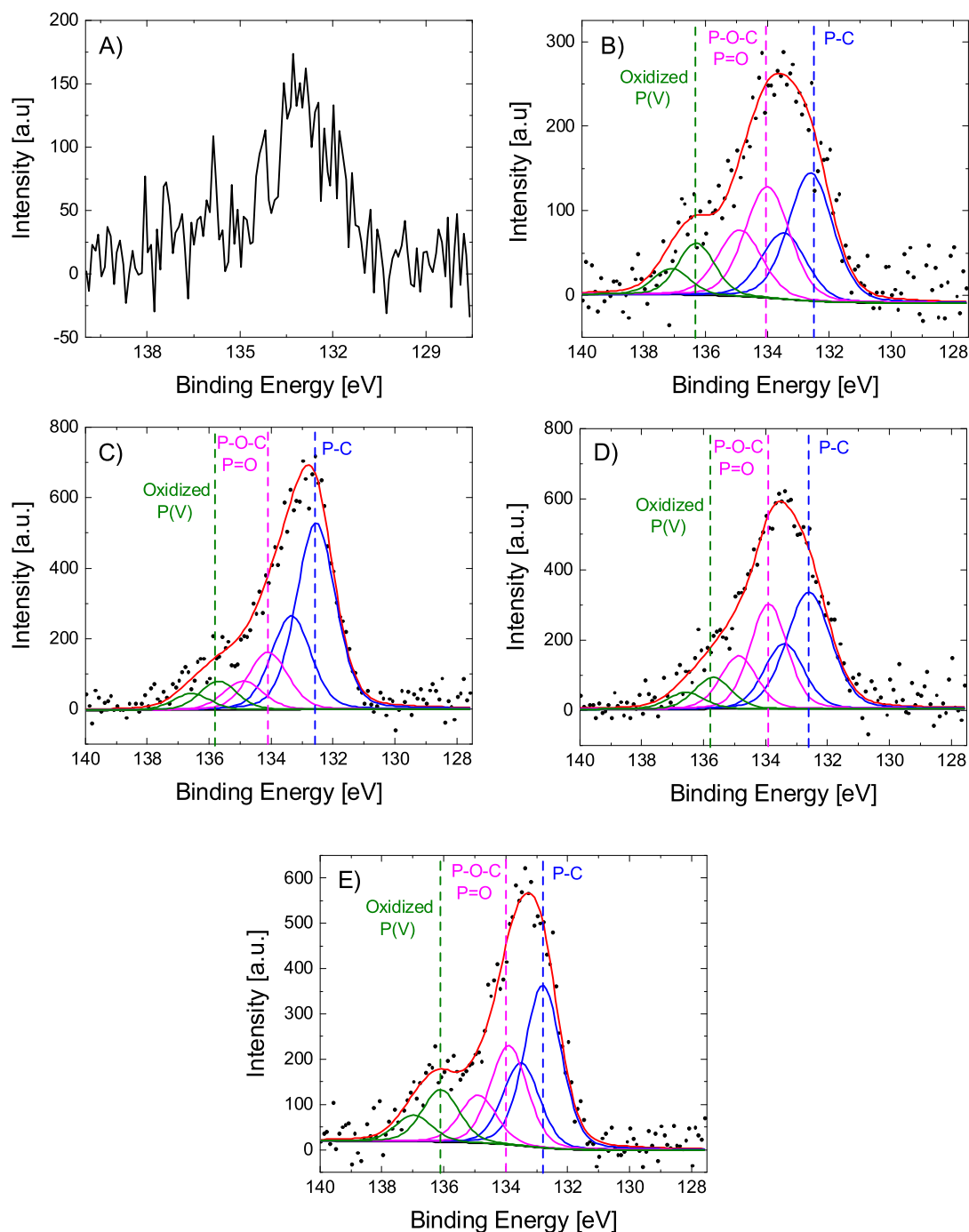
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Fig. 5. XPS spectra for P2p. A) MWCNTs-Ph$_2$PCl-1.05, B) MWCNTs-Ph$_2$PCl-1.2, C) MWCNTs-Ph$_2$PCl-1.33, D) MWCNTs-Ph$_2$PCl-1.55 and E) MWCNTs-Ph$_2$PCl-1.8.

in the total amount of phosphorus maintains mostly the same proportion even at high upper potential limits, showing the control in the P-species incorporated and the similar contribution of the different reactions. In contrast, the incorporation of chlorine shows an exponential increase with the upper potential limit (see Fig. 7-B), although the amount incorporated remains below the P content until the highest potential studied. The results show that the Ph$_2$-PCl can be easily incorporated into the MWCNT after the formation of the radical cation and that further reactions with nucleophiles or residual water gives rise to Cl removal as HCl, but at high potentials, for higher concentrations of the radical cation, the incorporation of Cl to the MWCNT is more probable.

Based on the results obtained by XPS, the presence of P—C bonds can suggest that during the modification of MWCNTs, the polarization of the electrode produces the oxidation of Ph$_2$PCl with formation Ph$_2$P^{+}Cl radical cation (step 1 in scheme 1). Subsequently, the highly electrophilic phosphoniumyl radical formed after the abstraction of one electron of the central phosphorus atom, interacts with the carbon nanotube generating an attack of the P moiety to the aromatic ring of the CNT structure, promoting a covalent coupling through the formation of a P—C bond (step 2 in scheme 1). Then, unstable Ph$_2$P˙Cl(MWCNT) complex tethering might generate two possible reactions in which the chlorination of the MWCNTs can take place to form Ph$_2$P˙(MWCNT-Cl) (step 3.1 in scheme 1), as well as, a second electron transfer (step 3.2
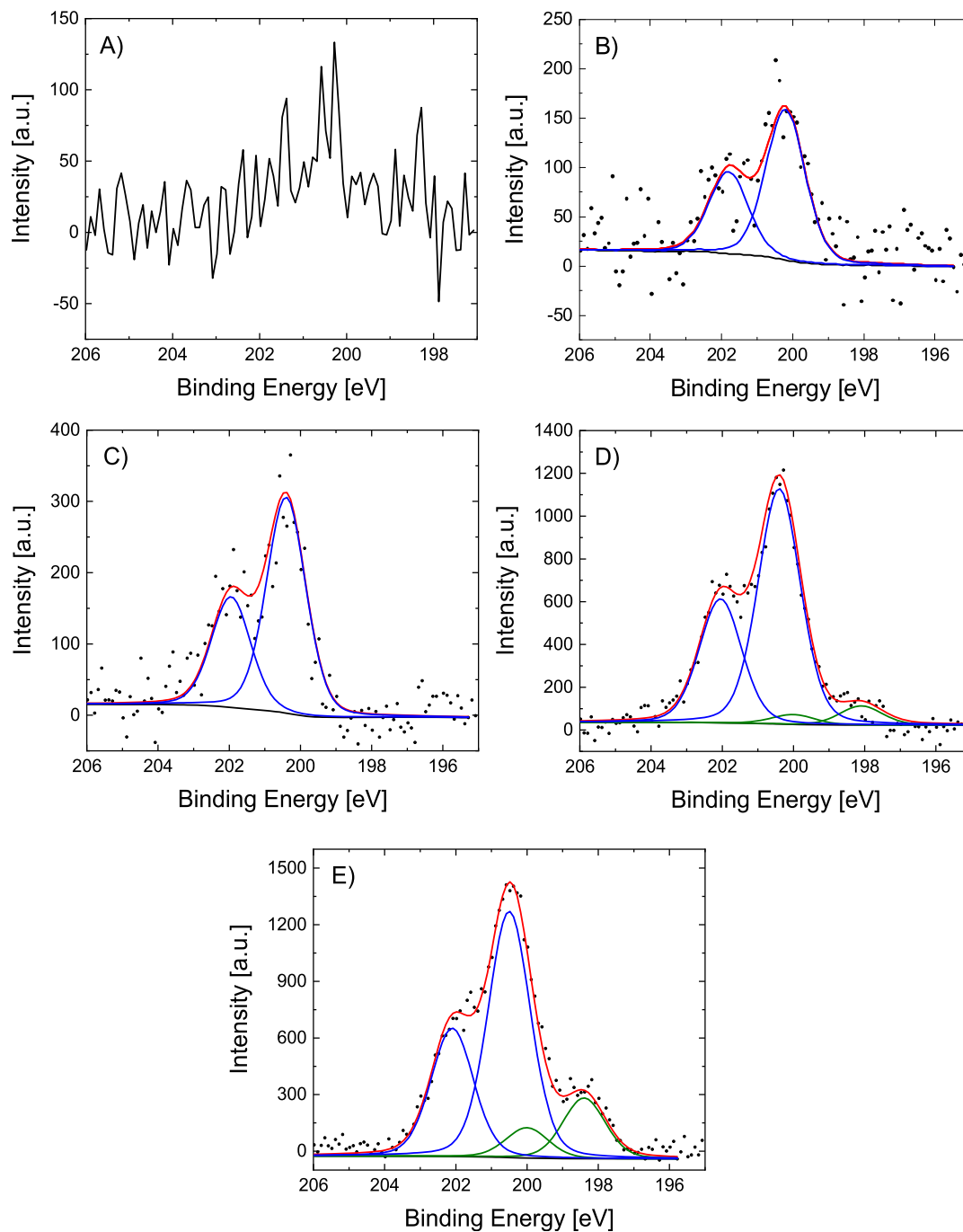
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Fig. 6. XPS spectra for Cl2p: A) MWCNTs-Ph$_2$PCl-1.05, B) MWCNTs-Ph$_2$PCl-1.2, C) MWCNTs-Ph$_2$PCl-1.33, D) MWCNTs-Ph$_2$PCl-1.55 and E) MWCNTs-Ph$_2$PCl-1.8 V.

Table 2
Chemical composition obtained from XPS of the electrochemical modified MWCNT- Ph$_2$PCl -X.

Upper potential limit[V vs. Ag/AgCl (3 M KCl)]	P at%	Cl at%	P/Cl	% P—C	% O—P—C / P=O	% P (V)	% Cl-C	% Cl⁻	Faradic efficiency (%)
1.05	0.38	0.09	4.3	*	*	*	*	*	0.8
1.20	0.61	0.18	3.4	45	41	15	100	*	0.6
1.33	1.25	0.54	2.3	69	21	10	100	*	0.8
1.55	1.28	0.98	1.3	51	38	12	87	13	0.4
1.80	1.77	2.49	0.7	52	31	17	81	19	0.5

* species not detected.

in scheme 1), oxidizing the central phosphorus atom to produce stable Ph$_2$PCl(MWCNT) and Ph$_2$P(MWCNT-Cl) species, this last one with PPh$_3$-like fashion (see Scheme 1-Step 4) [30,36]. Latest results are in agreement with the binding energy observed for the P—C bond and the presence of chlorine species.
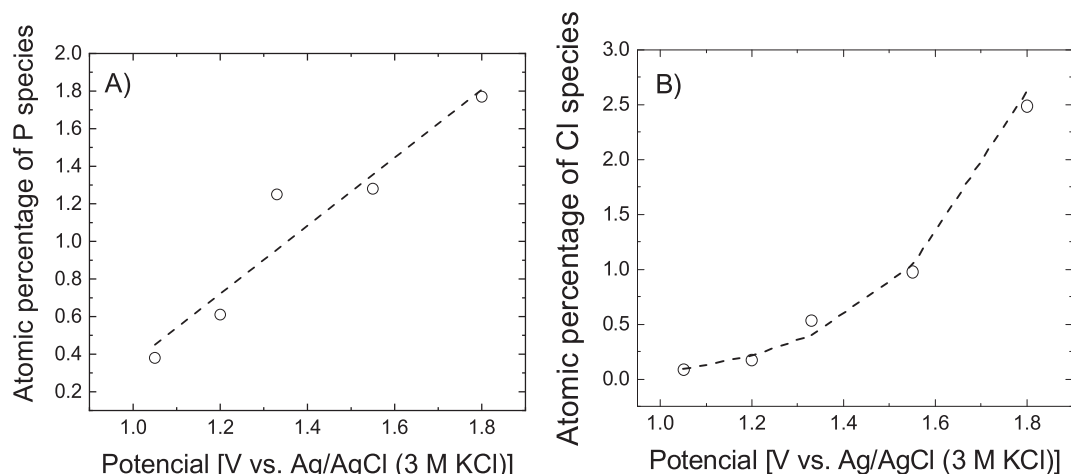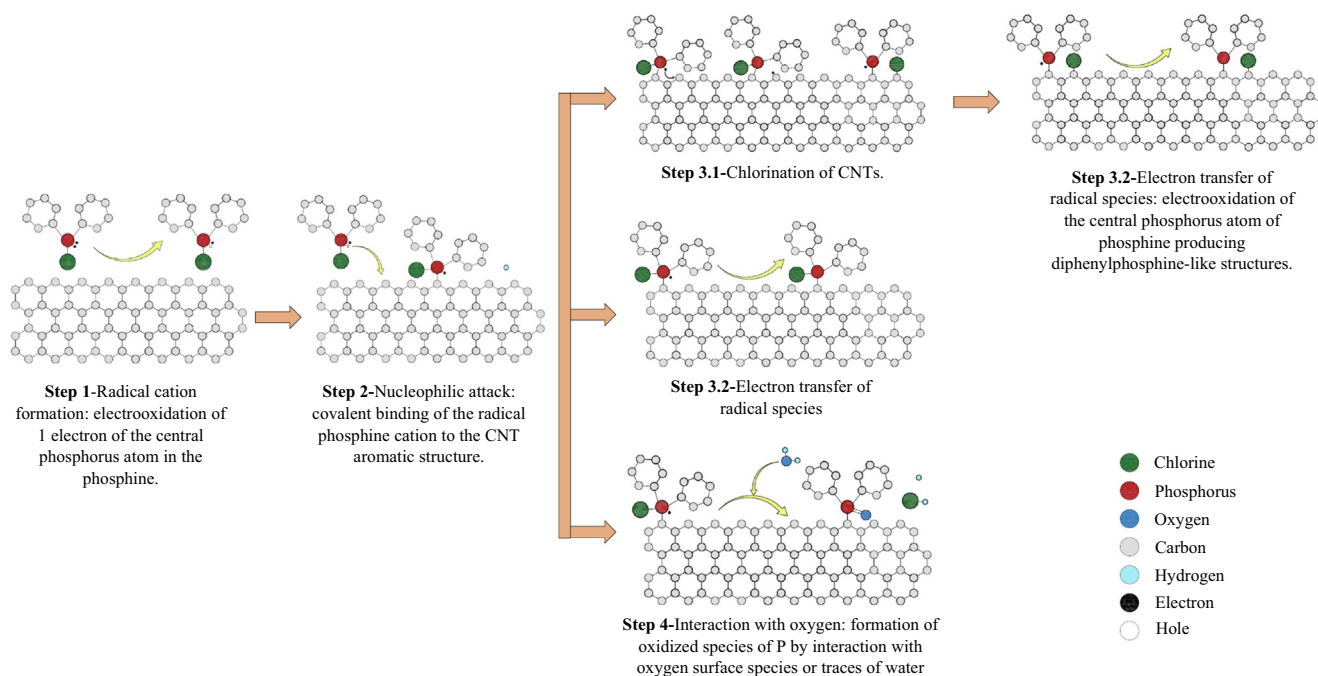
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Fig. 7. Amount of P and Cl incorporation with the upper potential limit during the electrochemical modification of MWCNTs with Ph$_2$PCl: A) Phosphorus content and B) Chlorine content.

Scheme 1. Scheme of the proposed mechanism for the electrochemical functionalization of MWCNTs with chlorodiphenylphosphine.

3.4. Effect of the surface oxygen groups in the functionalization of MWCNTs with Ph$_2$PCl

To analyze the effect of the presence of surface oxygen groups in the electrochemical functionalization of MWCNTs with Ph$_2$PCl, the electrochemical oxidation was performed using oxidized MWCNTs (o-MWCNTs). Fig. 8-A and B show the cyclic voltammograms of the o-MWCNTs in absence (black line) and presence (red line) of Ph$_2$PCl at 1.3 V and 1.8 V. Previously, open stepwise potential study was carried out to study the different upper potential limits (see Figure S4 in supporting information).

The electrodes of o-MWCNT oxidized in absence of the Ph$_2$PCl showed the normal quasi-rectangular shape of a carbon material typically observed in organic medium. Once the o-MWCNTs is oxidized in presence of Ph$_2$PCl, an oxidation current is clearly observed and ascribed to the oxidation of Ph$_2$PCl. Unlike MWCNTs, the two oxidation processes A$_1$ and A$_2$ are better defined in the o-

MWCNTs and showed potential peaks at around 0.8 and 1.6 V, respectively (see Figure S5 in supporting information). The electron transfer of the modified o-MWCNTs has been also studied in presence of Fe[(CN)$_6$]$^{3-}$/$^{4-}$ redox couple (Fig. S6). It can be observed that the electrochemical functionalization of the o-MWCNTs with phosphine produces an increase in the potential peak separation and then, a decrease in the electron transfer constant from around 3×10^{-5} m s^{-1} to 1.5×10^{-5} m s^{-1}. However, it must be noted that the effect of the functionalization potential is not as important as with the non-oxidized MWCNT, thus suggesting that with increasing the degree of oxidation, the reactivity of the functional groups increases. This may favor both the reaction with the phosphine molecule and the removal oxygen groups through further electrochemical oxidation. In any case, the effect of the amount and type of oxygen groups should be studied in detail.

XPS analysis for P and Cl shows that their incorporation takes place at both potentials 1.3 and 1.8 V. The content of P in the o-
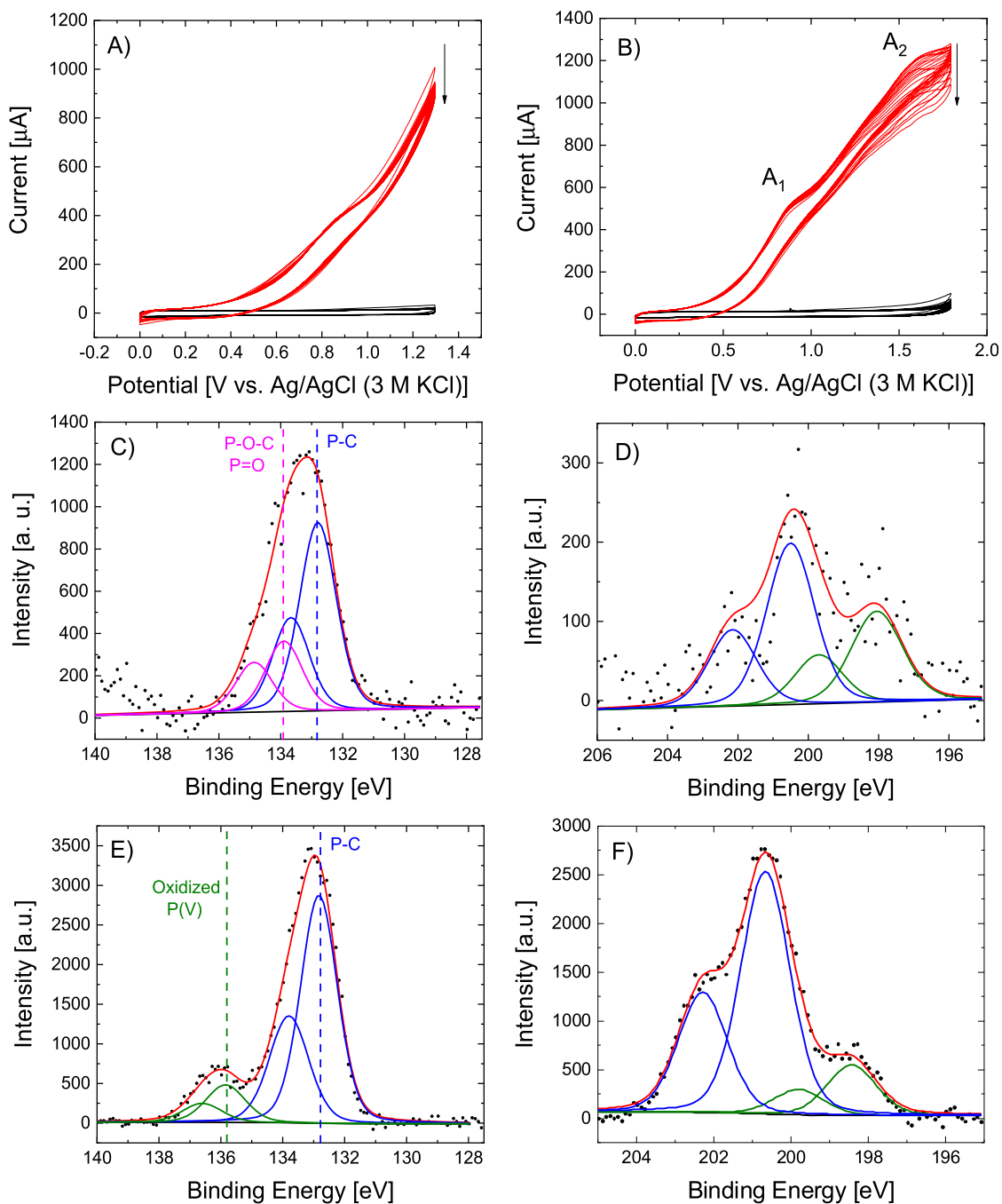
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Fig. 8. Cyclic voltammograms for o-MWCNTs at different upper potential limits: A) 1.3 V and B) 1.8 V in absence (black line) and presence (red line) of 0.1 M Ph$_2$PCl in MeCN at 50 mV s^{-1}, under inert atmosphere for 30 min of cycling. XPS spectra for o-MWCNT- Ph$_2$PCl-1.3: C) P2p and D) Cl2p. XPS spectra for o-MWCNT- Ph$_2$PCl-1.8: E) P2p and F) Cl2p.

MWCNT is considerably higher than the obtained with MWCNTs, the double in the case of the potential of 1.8 V, than in the non-oxidized MWCNTs, as can be observed in Table 3. This can be due to two possible reasons. The first one is related to the increase of the specific surface area after the oxidation treatment of the MWCNT. The second possible explanation might be consequence of the generation of radical species on the o-MWCNTs due to the removal of the surface oxygen groups, such as carboxylic acids,

Table 3
Chemical composition obtained from XPS of the electrochemical modified o-MWCNT- Ph$_2$PCl -X.

Upper potential limit [V vs. Ag/AgCl (3 M KCl)]	P at%	Cl at%	P/Cl	% P—C	% O—P—C / P=O	% P (V)	% Cl$_x$C$_y$	% Cl inorganic	Faradic efficiency (%)
1.30	0.99	2.37	0.42	70	30	*	62	38	0.4
1.80	1.69	0.92	1.84	85	*	15	83	17	0.6

* species not detected.

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that may occur at positive polarization of the electrodes, thus promoting the reaction with the phosphine radical cation, mainly generating covalent P—C bonds. Some additional reaction between the phosphine-containing species and oxygen groups cannot be discarded [34], producing oxidized species of P(V). Moreover, the faradic efficiency in the electrochemical modification is similar to the obtained with the pristine MWCNTs. Concerning the chlorine, the higher concentration of surface oxygen species in the o-MWCNTs favors the releasing of the chlorine atoms as HCl, according with Eq. (5), in agreement with the low halogenation observed in the o-MWCNTs.

4. Conclusions

Electrochemical functionalization of MWCNT and o-MWCNT with organophosphorus was achieved in organic medium employing electrochemical oxidation of chlorodiphenylphosphine by cyclic voltammetry. Formation of phosphoniumyl radical species by anodic polarization produces an electrophilic attack to the carbon atoms of the carbon nanotubes promoting a covalent attachment of the chlorodiphenylphosphine on the substrate through P—C bond. This process was accompanied by halogenation of the carbon nanotubes due to the chlorine species released in the phosphine-compound oxidation process. Upper potential limit demonstrated an important influence in the degree of P and Cl incorporation. The presence of the P-containing functional groups on the CNTs resulted in an decrease in the efficiency of the electron-transfer for the redox couple $Fe[(CN)_6]^{3-/4}$ in comparison with the pristine MWCNTs, as consequence of the hindrance of the P-functional groups incorporated, that increase the irreversibility of the redox process; however, if the functionalization potential increases an improvement of the electron-transfer rate is produced as consequence of the oxidation of the functionalities introduced on the MWCNTs. Characterization of the functionalized CNTs surface demonstrated that anchoring of the phosphoniumyl radical generates a diphenylphosphine-like structure and that when upper potential limit increases the oxidation of the P(III) species occur. Interestingly, the increase of the upper potential limit causes an increase in the incorporation of both species (P and Cl), and in particular P-doping prevails over the chlorine which can participate in secondary reactions that limit its incorporation. Presence of surface oxygen groups on the carbon nanotubes favors the direct anchoring of the phosphine radical cation to the carbon nanotube through P—C bonds, at the same time that halogenation of the carbon nanotubes is importantly suppressed.

CRediT authorship contribution statement

Andrés Felipe Quintero-Jaime: Conceptualization, Methodology, Investigation, Writing – original draft. **Alessio Ghisolfi:** Methodology, Investigation, Writing – original draft. **Diego Cazorla-Amorós:** Conceptualization, Methodology, Supervision, Writing – review & editing, Funding acquisition. **Emilia Morallón:** Conceptualization, Methodology, Project administration, Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2022.05.125.

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