

Defective bimetallic Pt-Ni/graphene catalysts by one-step or two-step low-pressure plasma processing

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Low-pressure plasma, Pt-Ni catalysts, defective nanoparticles, graphene, fuel cells

Abstract

One appealing strategy in order to reduce the use of critical raw metals in catalyst materials, such as platinum group metals, is to synthesize nanocomposites based on defective and/or bimetallic nanoparticles anchored to high surface area carbon matrices. In this work, Pt-Ni nanoparticles on graphene nano-platelets catalysts are synthesized by an original methodology based on low-temperature plasma treatments of solid precursors. Specifically, we optimized a one-step treatment (T_1), in which a powder mixture comprising graphene, nickel acetylacetonate and platinum acetylacetonate organometallic precursors are simultaneously treated in an oxygen plasma discharge. We also investigate a two-step (T_2) approach, in which the Ni and Pt precursors are sequentially treated to first nucleate Ni particles acting as preferential germination sites for the Pt nanoparticles. Both approaches lead to the effective degradation of the precursors to form Ni and Pt based nanoparticles anchored to the graphene sheets. The resulting bimetallic catalysts have been characterized by electron microscopy (STEM/TEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and X-

ray photoelectron spectroscopy (XPS) showing that the plasma treatment conditions strongly affect the nanoparticles morphology and their oxidation state. While the T₂ treatment leads to well-defined small aggregates of Ni(OH)₂ and Pt nanoparticles of 2-3 nm, T₁ leads to the formation of single phase domains up to 10 nm containing Pt, Ni, NiO or Ni(OH)₂. The electrochemical properties investigated by CO stripping and oxygen reduction reaction (ORR) activity measurements show a similar catalytic activity for the two catalysts with a marked contribution associated to structural defects present at the Pt-Ni grain boundaries. Such highly defective nanoparticles are thus promising for catalysis applications such as in proton exchange membrane fuel cells.

1. Introduction

In order to lower the environmental impact associated with the ever growing energy consumption, it is urgent to develop more sustainable and efficient energy devices. This is particularly true for the automotive industry, for which proton-exchange membrane fuel cells (PEMFCs) is a key technology to reduce the direct greenhouse emission as water and heat are the only direct products of the reaction.¹ Another advantage associated with the PEMFC technology comes from its relatively high efficiency and easy integration in transportation systems. Besides this, the upscaling of the PEMFCs technology is still limited by the high production cost and the insufficient lifetime. Moreover, Duclos *et al.*² recently showed that only a low percentage of the platinum used worldwide is recycled, while the platinum loading in the catalytic layer of PEMFCs can be up to 40 wt.%. Large-scale manufacturing of PEMFCs requires thus to develop new methods to reduce the noble metal loading while preserving the devices efficiency. One possible solution is to deposit defective or core-shell nanoparticles in which a fraction of Pt is replaced by a more abundant and cheaper metal such as nickel, cobalt, etc.^{3,4} Bimetallic particles not only allow to decrease the noble metal content, but also result in the enhancement of the catalytic activity and stability over cycling.⁵⁻⁷ As conventional processing of catalysts by solutions involve an extensive use of solvents, new methods have been recently explored to deposit catalyst materials on various high surface nanomaterials based on plasmas or plasma assisted treatments.⁸⁻¹⁴ In particular, we recently proposed a new method to deposit Pt/C catalysts using a direct low-pressure radio-frequency (RF) oxygen plasma to treat a solid (powder) mixture comprising platinum-acetylacetonate and carbon black.¹⁵ The main advantages of the "dry" plasma processing rely on its high versatility, namely

by selecting the adequate plasma chemistry and treatment conditions,¹⁶ its low-energy consumption, low environmental impact (solvent-free) and its potential to be up scaled. Moreover, the absence of contamination from solvent residuals is beneficial for avoiding poisoning effects on noble metal particles.¹⁷ In this work, we apply an optimized RF oxygen plasma treatment to synthesize bimetallic Pt-Ni/C catalysts. Our precursor materials are high surface area graphene nanoplatelets, Ni acetylacetonate and Pt acetylacetonate powders. In order to deposit bimetallic particles, we explored two strategies based on the sequential (two-step, T₂) or the simultaneous (one-step, T₁) treatment of the Ni and Pt organometallic precursors. The catalysts were characterized by combining multiple state-of-the-art analytical techniques such as X-Ray diffraction (XRD), scanning transmission electron microscopy (STEM/TEM) coupled with energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Electrochemical characterizations were carried to compare the catalytic performance of the materials through the investigation of CO stripping voltammograms and measurements of the oxygen reduction reaction (ORR) activity.

2. Materials and methods

The synthesis starts with the mixing of the powder precursor including one or both organometallic precursors, i.e. nickel (II) acetylacetonate (Ni(acac)₂, C₁₀H₁₄O₄Ni, Strem Chemicals) and platinum (II) acetylacetonate (Pt(acac)₂, C₁₀H₁₄O₄Pt, Strem Chemicals) and the nanostructured carbon substrate, i.e. graphene nanoplatelets, (GNP, Strem Chemicals), having an average lateral size of ~5 μm, a thickness of ~6 nm and a surface area of ~150 m²/g. The powder mixture is then introduced in a cylindrical low-pressure plasma reactor and treated in a RF (13.56 MHz) inductively-coupled plasma (ICP) discharge. The metal loading was fixed to 15 wt.% of Pt and 5 wt.% of Ni. The reactants were dispersed uniformly in a glass petri box and treated under stirring conditions. In order to investigate the precursor degradation and the following nanoparticle nucleation, two treatment strategies have been compared; in the one-step approach (T₁), both organometallic precursors (and GNP) are simultaneously exposed to an oxygen plasma treatment. In the two-step treatment (T₂), the Ni precursor and GNP are first treated following the low-energy oxygen plasma to deposit Ni seed particles (T_{2A}), then, the Ni/GNP catalyst is taken out of the chamber, Pt acetylacetonate is added to the mixture and the second treatment (T_{2B}) is operated to degrade it and nucleate Pt nanoparticles. The two strategies are schematically shown in **Figure 1**.

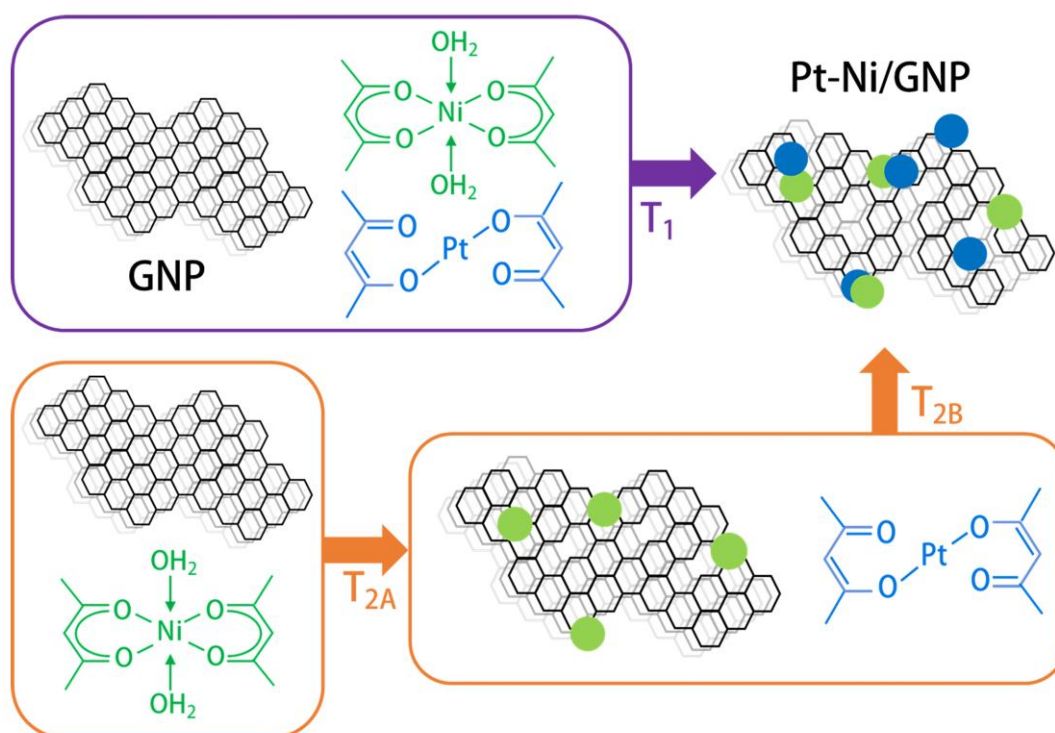


Figure 1. Sketch of the one-step (T_1) and two-step (T_2) processes for the plasma synthesis of Pt-Ni/GNP catalysts.

The oxygen flux injected into the plasma chamber was fixed to 5 sccm and the plasma conditions are the following: in T_1 and T_{2B} , the treatment starts with low-energy pulsed plasma treatment (40 min at 80 W, duty cycle 50%, frequency 10 Hz) immediately followed by a short and energetic treatment (8 min at 100 W followed by 5 min at 150 W). These conditions have been optimized in our lab to effectively degrade the organic part of the precursors while avoiding the coalescence or etching of metal nanoparticles (occurring for excessively energetic treatments). In T_{2A} , the low-energetic pulsed oxygen plasma treatment is applied to initiate the nucleation of Ni nanoparticles under the same conditions as for T_1 . The organometallic precursor's degradation and the formation of metal nanoparticles were investigated by X-ray diffraction (XRD, X'Pert PRO PANalytical®). The particles morphology and composition were investigated by transmission electron microscopy (TEM/STEM, Tecnai Osiris, by Thermo Scientific) equipped with EDX. The particles size distribution was determined by using the image processing software ImageJ®. The surface analysis was performed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi by Thermo Scientific) using monochromatized Al K-alpha X-ray source, equipped with a dual ion-electron flood gun. High-resolution C 1s, O 1s, Ni 2p and Pt 4f core levels spectra were acquired at 30 eV pass energy, while the scan number was adjusted from 8 to 32 scans to get similar signal-to-noise ratios. The electrochemical properties were investigated in a three-electrode cell at room temperature

with a reversible hydrogen reference electrode (RHE), water and perchloric acid electrolyte solution (HClO_4 , 0.1 M) and the catalytic layer deposited on a rotating glassy carbon (GC) disk as the working electrode. The 10 μL of the catalyst ink comprising ultrapure water isopropanol and 5 wt.% Nafion® solution were deposited on the GC disk to get a Pt loading of $40 \mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$. To ensure that all the pores were filled, a drop of electrolyte was firstly deposited onto the catalytic layer, to cover the entire catalytic layer, then, the electrode was put under vacuum in order to outgas the layer by bubbling air through the drop. Once no more air bubbles were visible, the electrode and the drop were put back at atmospheric pressure so that the drop filled the empty porosity of the layer, which ensured the full wetting of the catalyst. This procedure allows achieving stable and reproducible electrochemical characterizations thanks to the full wetting of the metal particles by the electrolyte.^{18–20} Voltammetry cycles were acquired between 0.05 and 1.23 V vs. RHE at $0.5 \text{ V} \cdot \text{s}^{-1}$ and $0.02 \text{ V} \cdot \text{s}^{-1}$ rates. The electroactive surface area was determined by CO stripping.^{21–23} The electroactive surface area was calculated from the CO oxidation peak current.²⁴ The chemisorbed CO at the working electrode surface was electrooxidized into CO_2 by increasing the electrode potential from 0.05 to 1.23 V vs. RHE at $0.02 \text{ V} \cdot \text{s}^{-1}$. The activity of the catalysts for the oxygen reduction reaction (ORR) was measured on a rotating disk electrode setup between 0.4 and 1.05 V vs. RHE at $0.001 \text{ V} \cdot \text{s}^{-1}$ at 1600 and 2500 rpm rotating speeds. The two respective kinetic current values (one for each rotation speed) were averaged in order to obtain the kinetic current of the catalysts. The values of this averaged kinetic current were divided by the electroactive surface of the catalysts in order to obtain the specific activity of the catalysts ($\text{A} \cdot \text{m}_{\text{Pt}}^{-2}$). In order to compare the catalysts activity was visually compared by Tafel plots expressed as a function of the logarithm of the specific activity. In addition to the specific activity (SA), the mass activity (MA) was calculated by dividing the averaged kinetic current by the total Pt mass on the electrode derived from previous ICP-OES measurements on the catalyst powder. The electrochemical results were compared with a reference commercial catalyst (Pt/C Tanaka 37 wt.%) measured in the same conditions. More technical details about the procedure can be found in Supplementary Information.

3. Results and discussion

Electron microscopy images are investigated to get insights into the nanoparticles nucleation mechanism during the plasma treatment. For the one-step catalyst (T_1), the final morphology is rather complex; high-resolution TEM images show that some particles present fringes from

crystallographic planes while others result in a different contrast and do not show fringes (**Figure 2a**). The nanoparticles size distribution is rather wide, extending from 1-2 nanometers up to 5-6 nm. Complementary investigations with HAADF STEM confirm the very complex while reproducible morphology characterized by nanostructured domains extending up to 10 nm (**Figure 2b**). In STEM, the atomic number of the element markedly influences its greyscale contrasts, so the contrast difference in **Figure 2b** indicates a strong variability of the composition of the interconnected nanoscale domains. This is confirmed by EDX maps showing that Ni and Pt species form rather complex interrelated nanostructured domains. A remarkably different morphology is obtained in the sequential treatment (two-step process) for which no particle coalescence is observed and well-dispersed and well-defined 1-3 nm particles decorate the graphene sheets (**Figure 3a** and **3b**). This uniform morphology suggests that Ni particles growth and the Pt particles nucleation and growth may preferentially occur on previously formed small Ni seeds acting as germination sites.^{7,25} Based on our knowledge from previous investigations, the T_{2A} treatment energy and duration are not sufficient to fully degrade the Ni precursor, so that only sub-nanometre Ni particles (hardly visible in TEM) are formed during T_{2A}. The Ni particles growth is thus expected during the following T_{2B} treatment. The comparison between the T₁ and T₂ catalysts morphology (**Figure 4**) suggests that in the one-step process, Pt and Ni particles nucleate simultaneously on anchoring sites on the graphene surface such as defects (carbon vacancies) or on oxygen functional groups,^{26,15} while in the two-step procedure, the plasma activated molecular fragments from the Pt precursor tend to preferentially nucleate on previously-formed small Ni particles resulting in the formation of small Pt-Ni particles aggregates (the plasma energy being not sufficient to form alloys). Overall, the plasma processing involves the formation carbon defects and oxygen surface groups, the fragmentation of Ni and Pt precursors (which may be sensibly different because of the different melting temperature and oxygen affinity) and nucleation/growth of Pt and Ni particles.

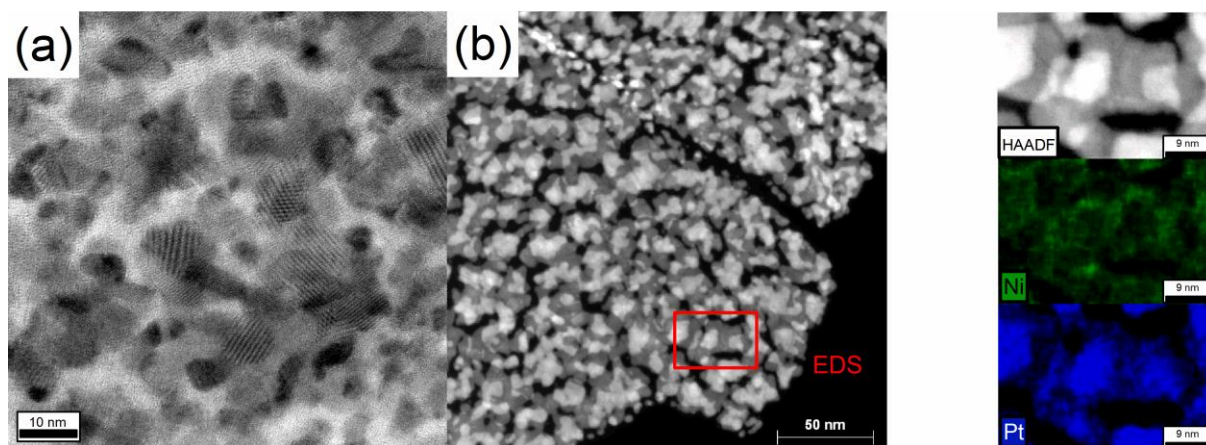


Figure 2. Characterization of the Pt-Ni catalysts made following the one-step treatment of the organometallic precursors (T_1). (a) HR-TEM image. (b) STEM image and EDX map performed on a selected region to get visual insights on the distribution Pt and Ni atomic species.

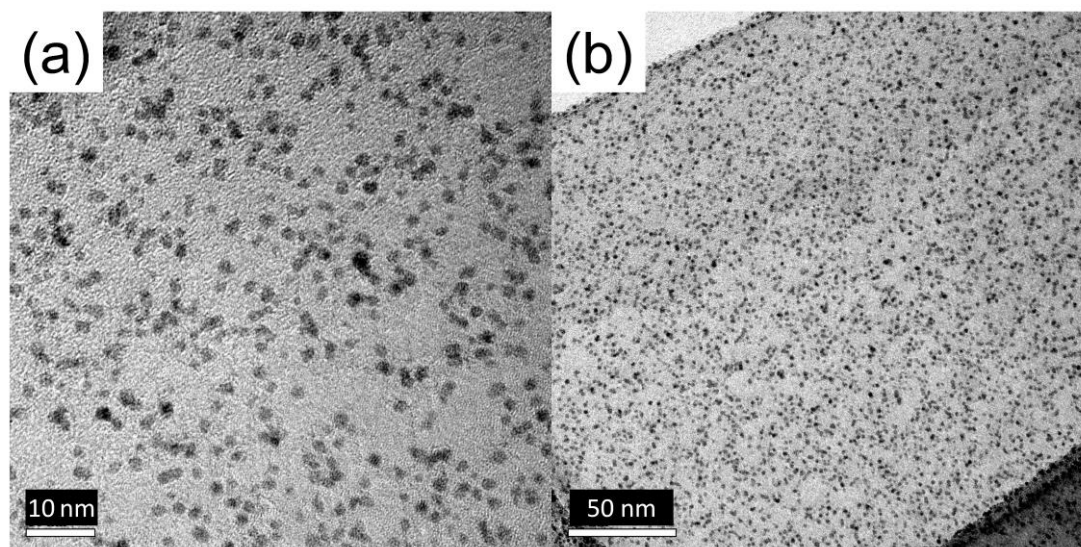


Figure 3. Bright field TEM images of the Pt-Ni/graphene catalyst made following the two-step treatment (T_2). The high magnification image (a) shows the presence of well separated particles of 1-3 nm, the lower magnification image (b) shows the homogeneity of the particles dispersion of graphene sheets.

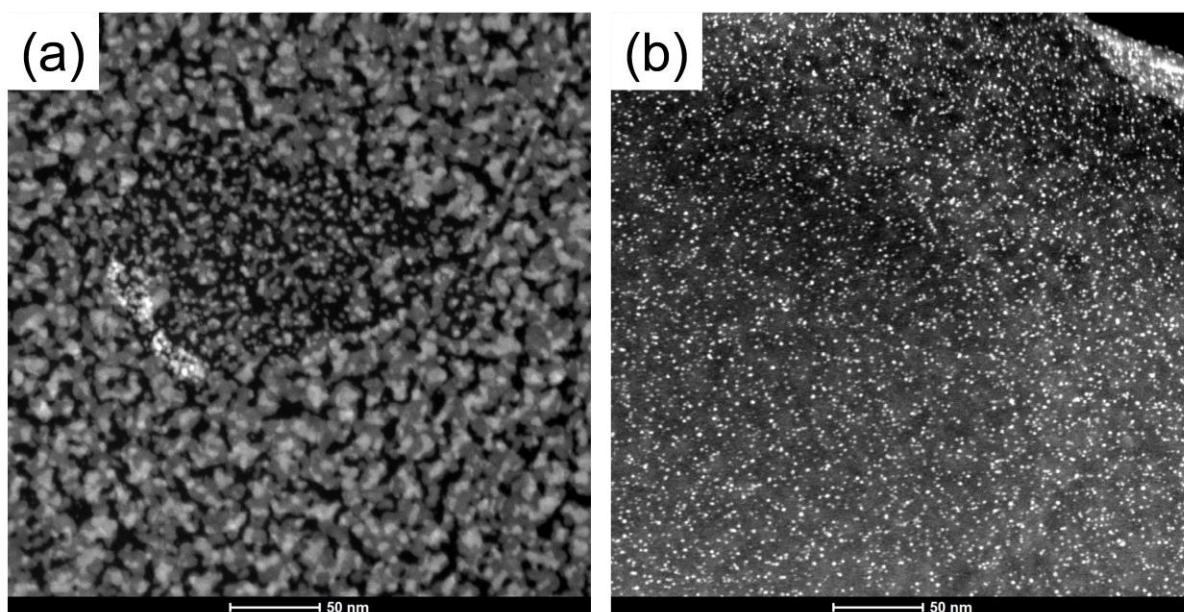


Figure 4. High angle annular dark field (HAADF) STEM of the Pt-Ni catalysts fabricated following (a) the simultaneous treatment of the two organometallic precursors (T_1) and (b) the sequential treatment of the nickel and then the platinum precursors (T_2).

The precursor degradation and the nanoparticles formation in T_1 and T_2 treated catalysts were analysed by XRD (**Figure**); the diffraction patterns are visually compared by normalizing the intensity of the graphene (111) peak at $2\theta=27^\circ$. Both for T_1 and T_2 plasma treatments we observe the almost complete disappearance of the characteristic pattern of the non-treated metal acetylacetonates and the simultaneous appearance of broad diffraction peaks ascribed to cubic Pt.²⁷ Precursor traces are slightly more evident in T_2 which also displays a weaker Pt peak intensity with respect to T_1 (although with very a similar FWHM). Interestingly, no NiO or Ni(OH)₂ phases are observed despite of the fact that oxygen was constantly flown into the plasma discharge. Overall, XRD results indicate that for T_1 and T_2 , the Ni particles are amorphous. Other experiments (not shown here) have evidenced that crystallized NiO domains are formed only with sensibly higher discharge power (above 200 W), however, these extreme conditions were not explored on graphene-based catalysts to avoid introducing too much defects on graphene layers.

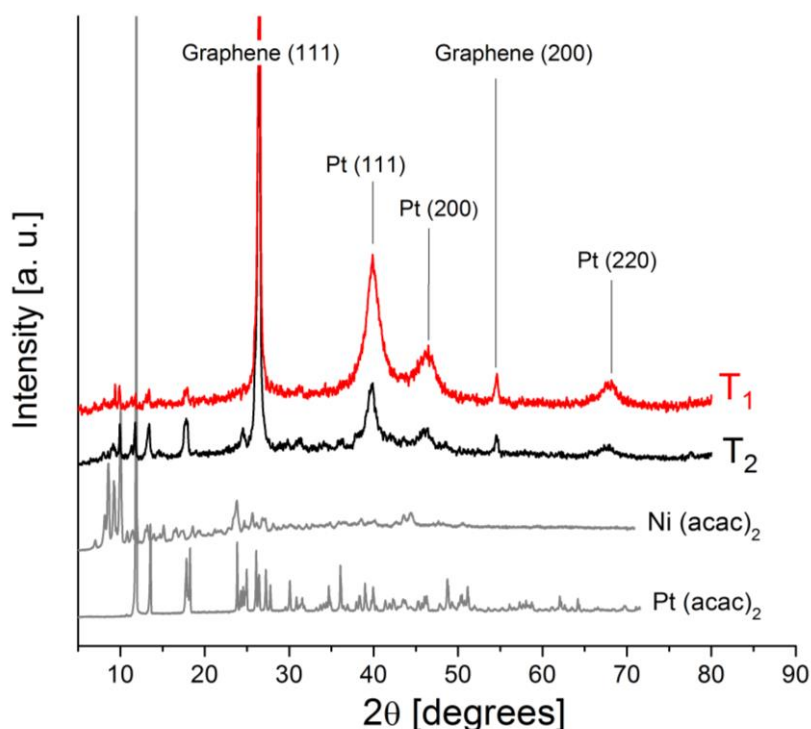


Figure 5. XRD patterns of the Pt and Ni organometallic precursors and the Pt-Ni/graphene catalysts treated by one-step (T_1) and two-step (T_2) plasma treatments.

The surface of the T_1 and T_2 catalysts was investigated by XPS by acquiring both survey and high-resolution Pt 4f, Ni 2p, C 1s and O 1s spectra (**Figure**) to derive the atomic % quantification and for chemical analysis. The one-step catalyst (**Figure a**) shows a single-component (Pt^0) asymmetric Pt 4f doublet spectrum centred at 70.8 (Pt 4f_{7/2}) and 74.1 eV (Pt 4f_{5/2}) binding energies; the peak asymmetry was previously fitted on a reference Pt electrode. The Pt 4f spectrum of the two-step catalyst clearly shows an additional shoulder component representing about 10% of the total peak area, at higher (+1.7 eV) binding energy (Pt 4f_{7/2} at 72.5 eV) ascribed to the presence of Pt hydroxide and/or to some residual precursor not fully decomposed by the plasma treatment. The three times higher Pt content in the T_1 catalyst possibly results from either a more complete degradation of the organometallic precursor or the different particle morphology, such as the presence of larger or flat (non-spherical) Pt domains. The line-shape of the Ni 2p doublet spectra (**Figure b**) (with the shake-up satellites peaks at 860.6 and 879.5 eV) and their binding energy indicate the dominance of nickel hydroxide Ni(OH)₂ state.²⁸ In the T_1 catalyst, however, we clearly see the contribution from Ni⁰ (Ni 2p_{3/2} at 852.5 eV) and we cannot exclude the presence of a weak NiO signal which would result in a Ni 2p_{3/2} component centred at ~853.5 eV and thus not easily discriminated.^{28–}

³⁰ The analysis of the O 1s spectra (**Figure c**) shows a main component located at about 531 eV ascribed to organic oxygen and Ni(OH)₂²⁸. The one-step catalyst features a higher metal oxide amount, as marked by the high binding energy shoulder peak at ~528.8 eV accounting for ~7% of the O 1s peak area. The higher oxygen affinity of Ni compared to Pt and the absence Pt oxide components in the Pt 4f spectrum allows to safely ascribe this shoulder peak to oxygen atoms in NiO. Interestingly, the two-step process does not result in the formation of Ni-O bonds. Finally, the C 1s spectra are not evidently affected by the treatment conditions (**Figure d**), with a main component (representing about 65% of the total peak area) from of C-C and C-H groups at 284.8 eV and a weaker contribution for carbon-oxygen functional groups (C-O, C=O and O-C=O representing about 20, 10 and 5% of the C 1s area, respectively).

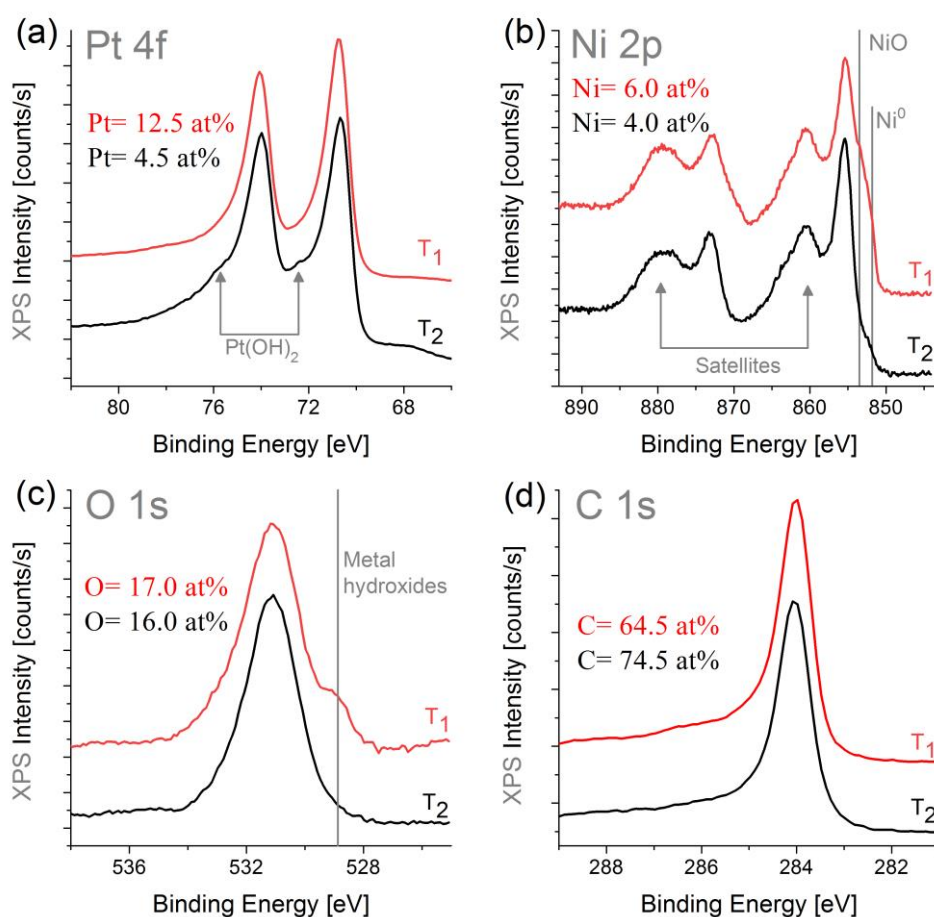


Figure 6. High-resolution XPS core level spectra of Pt 4f (a), Ni 2p (b), O 1s (c) and C 1s (d) after the one-step (T₁, in red) and the two-step (T₂, in black) plasma treatments.

The electrochemical properties of the T₁ and T₂ Pt-Ni/graphene catalysts are investigated by CO stripping and oxygen reduction reaction (ORR) activity measurements (with the corresponding Tafel curves). These properties are compared to those of a commercial Pt/C reference catalyst in **Figure 7**, showing the average results obtained with two different working electrodes prepared from the same catalyst ink. The CO stripping voltammograms are normalized to the Pt surface area measured on the electrode because of the substantially different Pt loading and electroactive Pt surface (**Figure 7a**). The voltammograms show a broad peak at about 0.70 V vs. RHE which is attributed to defective crystallites which is not observed in the reference Pt/C catalyst. This feature is associated to low-coordinated Pt atoms at the grain boundaries between Ni and Pt or at the interconnection area between the small nanoparticles aggregates observed in STEM images (**Figure 4**). The other peak around 0.82 V vs. RHE is ascribed to Pt particles with a size of around 3 nm or higher, or possibly to PtNi alloys.³¹ The electroactive surface area (S_{CO}) values obtained for T₁, T₂ and the Pt/C reference catalysts are 21, 18 and 109 m² g_{Pt}⁻¹. Taking into account the particles size, such a low electroactive surface area values obtained for the plasma catalysts is ascribed to the stacking of the graphene sheets on the rotating disk electrode that prevents the full wetting of Pt particles by the electrolyte. The ORR voltammograms acquired at 2500 rpm rotating speed are shown in **Figure 7b**. The associated Tafel plots are visually compared in **Figure 7c**; from the slope of the Tafel plots we see that for T₁ and T₂ catalysts we have a similar decay rate of 76 and 70 mV/dec which is higher than what is observed in the commercial catalyst (55 mV/dec). Taking into account the metal loading, the mass activity (MA) values at 0.95 V vs. RHE obtained for T₁, T₂ catalysts and the Pt/C reference measured in the same conditions are 2.3, 3.3 and 10.9 A·g_{Pt}⁻¹. Interestingly, the specific activity (SA) values at 0.95 V vs. RHE obtained for T₁, T₂ and the Pt/C reference catalysts are 0.011, 0.019 and 0.010 A·m_{Pt}⁻², respectively. The two step treatment results thus in the highest SA value. This may be due to two phenomena: (i) the presence of PtNi alloys at the surface of the nanoparticles and (ii) the higher density of structural defects, as shown by the higher intensity of the CO oxidation peak situated at 0.70 V vs. RHE. Indeed, it is well known that the presence of PtNi alloy and of a high density of structural defects at the surface of the nanoparticles improves the specific activity for the ORR.

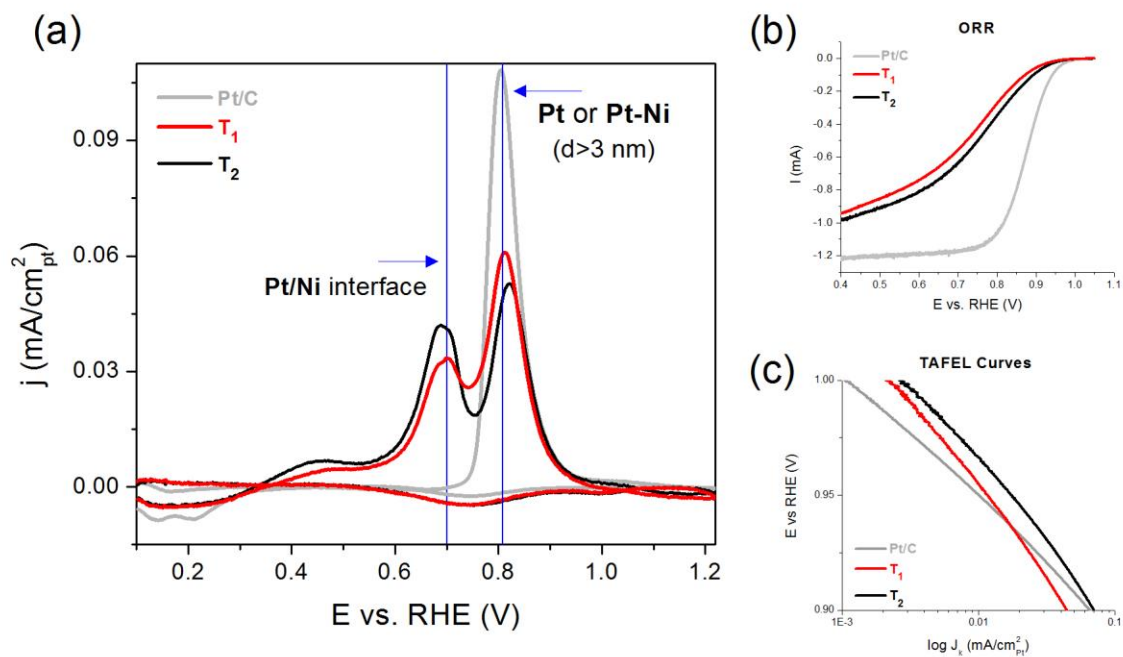


Figure 7. Electrochemical characterizations of the one-step (T₁) and two-step (T₂) Pt-Ni/graphene catalysts and the reference Pt/C catalyst. (a) CO Stripping voltammograms, (b) ORR voltammograms and (c) the derived Tafel plot.

4. Conclusions

In conclusion, defective bimetallic Pt-Ni nanoparticles were synthesized on graphene nanoplatelets by one-step (T₁) or two-step (T₂) low-pressure RF plasma treatments of solid precursors. The oxygen plasma allows the decomposition of the organometallic precursors and the formation of Pt and Ni nanoparticles anchored to the graphene substrate. The nanoparticles nucleation mechanism and the final morphology were related to the treatment conditions; namely, in the one-step process, Pt and Ni based particles simultaneously nucleate on graphene defects and grow to form a complex morphology of interconnected Ni⁰, Ni(OH)₂, NiO and Pt⁰ domains with a lateral size from few nm up to 10 nm. In the two-step treatment of the Ni and Pt precursors, homogeneously-distributed spherical Pt and Ni particles with a diameter of about 2-3 nm nucleate and grow preferentially in correspondence to the previously formed Ni seed particles to form small and stable aggregates of highly defective Pt-Ni particles. This last approach allows maximizing the grain boundaries area and reaching a high specific activity. Investigations are in progress to improve still limited active surface area as compared to the commercial Pt/C catalyst which may rely on the presence of non-anchored metal particles. However, this work shows that the plasma approach is promising for depositing controlled

defective particles almost without limitations on the carbon support or metal precursors; this flexibility potentially opens the way to broad applications of catalytic and energy materials.

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