

# Dispersed stabilized Pt nanoparticles synthesized from an organometallic precursor on Carbon Nanotubes

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## ABSTRACT

Carbon Nanotubes (CNTs) are novel types of nanostructured materials with unique structural, electrical and mechanical properties. In addition, carbon materials have been employed to support metallic nanoparticles (NPs) for electrochemical applications. In this work, we investigated the synthesis of platinum NPs starting from Pt<sub>2</sub>(dba)<sub>3</sub>, (dba= dibenzylideneacetone) synthesized in the laboratory and decomposed under H<sub>2</sub> atmosphere in THF in presence of hexadecylamine and functionalized Single-walled CNTs (SWCNTs). This method is a good alternative to disperse metallic NPs on SWCNTs. X-ray diffraction (XRD) analysis were carried out to study the structure of Pt/SWCNTs. High Resolution Transmission Electron Microscopy (HRTEM) studies revealed well dispersed and isolated platinum NPs (2-3 nm). Additionally, Infrared Spectroscopy measurements were used to study the presence of the stabilizer (HDA) on the surface of the Pt NPs.

**Keywords:** carbon nanotubes, Pt nanoparticles, organometallic.

## 1 INTRODUCTION

Carbon Nanotubes (CNTs) as a new class of carbon nanostructures have received numerous theoretical and experimental studies. Because of its nanometer size and attractive properties, CNTs are also of great interest for several applications, for example, batteries, flat panel displays, chemical sensor, etc. Additionally, high accessible surface area, low resistance and high stability suggest that CNTs are suitable materials for electrodes and catalyst supports in polymer electrolyte membrane fuel cells (PEMFC) [1]. The good properties of the catalyst supports, such as high surface area and high electrical conductivities, are essential for Pt catalyst to produce high catalytic activity [2]. As a result, carbon-supported platinum is the main type of electrocatalyst used for this proposes [3-5]. Pt

nanoparticles may decorate the external wall of the nanotubes, being deposited on single or multi-wall carbon nanotubes by chemical reduction method, mainly. The most employed precursors to prepare nanosized Pt particles on CNTs have been H<sub>2</sub>PtCl<sub>6</sub>, K<sub>2</sub>PtCl<sub>4</sub>, PtCl<sub>2</sub>, etc [6-8]. On the other hand, the use of PtMe<sub>2</sub>COD, (COD=1,5-cyclooctadiene) [9], Pt(acac)<sub>2</sub> [10,11], H<sub>2</sub>Pt(NO<sub>2</sub>)<sub>2</sub>SO<sub>4</sub> [12], Pt(dba)<sub>2</sub>, Pt(dba)<sub>3</sub>, (dba=dibenzylideneacetone)platinum [13] employing in different techniques, also result in the formation of uniformly dispersed nanoparticles with narrow size distributions.

In this paper, we will show that a high dispersion Pt nanoparticles on SWCNT can be obtained by optimizing the conditions of synthesis by an organometallic approach using Pt<sub>2</sub>(dba)<sub>3</sub> complex as precursor. The main concern in this paper is to investigate the effect of the presence of a long alkylchain amine (HDA) on the dispersion of Pt nanoparticles on SWCNTs.

## 2 EXPERIMENTAL

### 2.1 Pretreatment of Carbon Nanotubes

*First step.* Single-Walled Carbon Nanotubes (SWCNTs, Applied Nanotechnologies, Inc. 90-95% purity) were dissolved in 15 mL of HNO<sub>3</sub> (Sigma-Aldrich, 70 % ). After 30 seconds of ultrasonication, the solution was refluxed at 120 °C under constant agitation for 8 h. The solid phase was removed by centrifugation. After being washed with deionized water, the recovered SWCNTs were dried at 70 °C for 24 h.

*Second step.* The SWCNTs obtained in the previous step, were dissolved in 15 mL of HNO<sub>3</sub> (Sigma-Aldrich, 70 %): deionized water (10:1). After 30 seconds of ultrasonication the solution was refluxed at 120 °C under constant agitation for 10 h. The solid phase was removed by centrifugation, after being washed with deionized water.

## 2.2 Synthesis of Platinum Nanoparticles

The platinum precursor, Pt<sub>2</sub>(dba)<sub>3</sub> was prepared according to Monseley and Maitlis, using K<sub>2</sub>PtCl<sub>4</sub> as raw material [13]. Pt nanoparticles were synthesized and supported on commercial SWCNTs in situ under inert atmosphere using schlenk techniques as follows: the Pt<sub>2</sub>(dba)<sub>3</sub> precursor was added to distilled THF [14]. Thereafter, hexadecylamine, HDA (1 eq.) and SWCNTs (70 eq.) were added to the solution. Then, a dark brown solution was obtained and pressurized under hydrogen atmosphere (3 bar) for 20 h and the solution color turns dark brown into a homogeneous black solution. The resultant colloidal solution was purified by hexane washings (to eliminate the dibenzylideneacetone) and, finally, the purified concentrate black solution was evaporated in vacuum until the residue was completely dry. The difference between the approach used here and the adopted by Solla-Gullón et al. [15] that used similar precursor is the reduction method and the presence of a stabilizer.

## 2.3 Measurements

Fourier Transform-Infrared Spectroscopy (FT-IR, Spectrum One Perkin Elmer) was used to determine the presence of the HDA on the surface of the Pt nanoparticles after drying; KBr pellet (Aldrich, 99% IR grade) was employed to carry out this analysis. Powder X-ray diffraction data of the sample was collected using a Bruker Advance D8 diffractometer with Cu K<sub>α</sub> radiation, 0.02° min<sup>-1</sup> scan rate, from 2θ = 20 to 100°. A preliminary crystal mean size was calculated from the broadening of the (111) diffraction peak using Scherrer's equation:

$$t = \frac{0.9\lambda}{B \cos \theta_b} \quad (1)$$

where *t* is the crystal mean size, λ is the wavelength of the X-ray (0.15405 nm for Cu K<sub>α</sub>), B is the full width-at-half-maximum height of a diffraction peak at angle θ. Morphological, dispersion and average size studies were carried out by High Resolution Transmission Electron Microscopy (HRTEM, JEOL JEM-2010F Field Emission). A drop of the colloidal solution with no subsequent purification steps was deposited under argon on a holey carbon covered copper grid for TEM analysis.

## 3 RESULTS AND DISCUSSION

### 3.1 Characterization of Pt nanoparticles

Figure 1 shows FT-IR spectra of SWCNTs as-received, functionalized and with dispersed metallic nanoparticles.

From this figure, functionalized SWCNTs show peaks at 3530 and 1725 cm<sup>-1</sup> correspond to -OH and -COOH functional groups, respectively. There are also peaks around 1100 and 1160 cm<sup>-1</sup> corresponding to symmetric and asymmetric stretching bands of C-O-C of carboxylic groups according to Guzman et al. [12]. Commercial SWCNT without pretreatment spectrum is also presented as a reference showing some noising signals. As is well known FT-IR is a useful tool to verify the purity of commercial CNTs. It is clear that the commercial SWCNTs as-provided by the supplier company have impurities that may interfere in the process of the synthesis and support of the nanoparticles, for this reason, the commercial CNTs have to be pretreated before beginning the synthesis. Also, it is important to verify the purification of the commercial SWCNTs by FT-IR. In this Figure, we also show the spectrum of the system Pt-HDA-SWCNTs that is quite similar to the treated commercial SWCNTs with additional signals corresponding to amine group -NH<sub>2</sub> and C-H groups of alkyl chain from HDA. Coordination of amine groups to the surface Pt nanoparticles is confirmed with the slight displacement of the HDA signals (about 3330 cm<sup>-1</sup>).

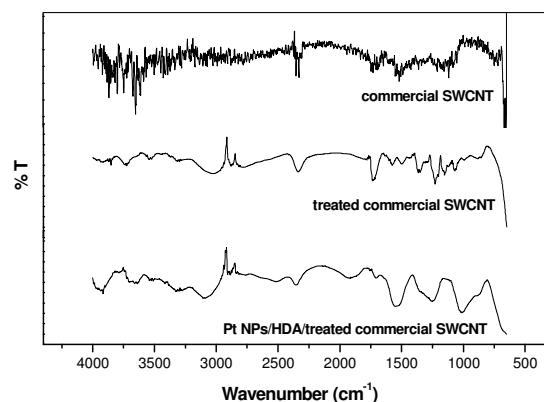


Figure 1. FT-IR spectra of commercial SWCNTs, functionalized SWCNTs and the Pt nanoparticles/HDA/functionalized SWCNTs system.

The X-ray powder diffraction (XRD) spectrum of stabilized Pt nanoparticles/SWCNTs is shown in Figure 2. The peaks at 39.7°, 45.5°, 67.6° and 81.6° can be assigned to Pt face-centered cubic (fcc) phase based on the data of the JCPDS file [04-0802] and corresponding to (111), (200), (220) and (311) crystalline plane diffraction peaks, respectively. The SWCNTs showed the typical peak of the (002) phase [16,17] of graphite. Some signals were assigned to PtO (JCPDS 43-1100), this specie could be produced on the surface during XRD analysis because the nanoparticles were exposed to the air. The rest of the signals were attributed to the HDA employed as stabilizer, which was in a 1:1 ratio respect to Pt. The broad of the peaks is related with the nanosize obtained.

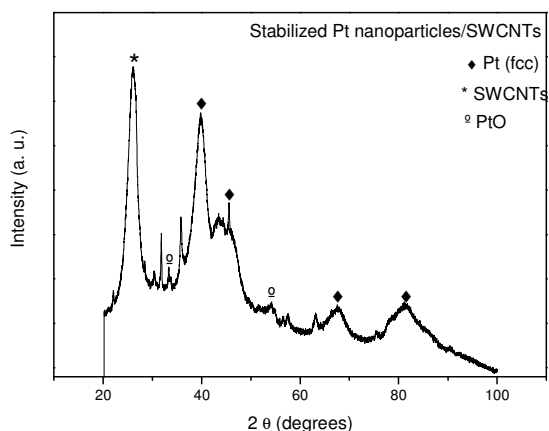


Figure 2. Powder X-ray diffraction pattern of stabilized Pt nanoparticles/SWCNTs.

The particle size obtained by Scherrer's equation was 0.2 nm. This result will be compared with those obtained by TEM analysis.

Typical high resolution transmission electron microscopy (HRTEM) images of the supported Pt nanoparticles are showed in Figure 3. It can be seen that Pt nanoparticles are well dispersed along SWCNT surfaces. The average platinum particle size was also determined from the images to be about 2-3 nm. Despite the small size of the Pt particles, particle agglomeration is rare, probably because the presence of HDA used as stabilizer. After analyzed the HRTEM images, it can be assured that the particles are on SWCNTs surfaces (Figure 2a). It seems that Pt nanoparticles tend to be preferentially attached where there is a larger concentration of carboxylic acid groups; additionally, the HDA seems to contribute to the well dispersion of the Pt nanoparticles. The morphology of the particles was revealed more clearly in Figure 2b. Pt particles exhibited semispherical morphology. This morphology is related to the presence of the alkylamine which displays an important role in the shape control of the particles, acting as a weak stabilizing agent and as a soft template [15]. Similar morphology was observed by Bayrakceken et al. from dimethyl(1,5-cyclooctadiene)platinum(II),  $\text{PtMe}_2\text{COD}$  as precursor on CNTs using a supercritical carbon dioxide deposition method [9].

According to the HRTEM results, the preliminary particle size calculated from DRX diffractograms (0.2 nm) presents a wide deviation of the values of histograms of size distribution from HRTEM micrographs (2-3 nm). These differences could be attributed to the support and stabilizer used.

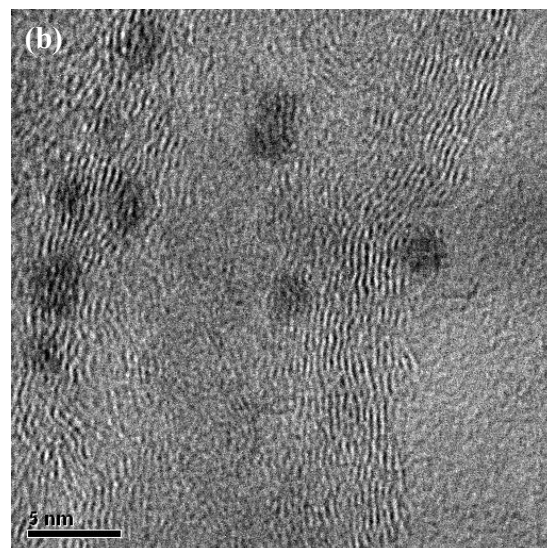
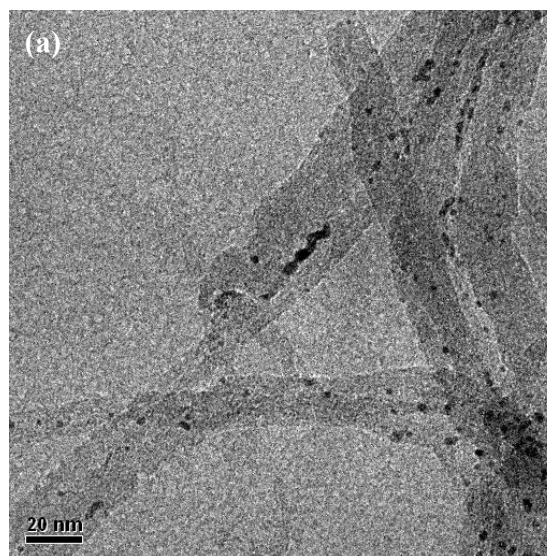


Figure 3. HRTEM Images of Pt nanoparticles (a) dispersed on SWCNTs (b) Higher magnification of Pt nanoparticles.

## 4 CONCLUSIONS

We have demonstrated that well dispersed Pt nanoparticles can be obtained on functionalized commercial SWCNTs using an organometallic approach from  $\text{Pt}_2(\text{dba})_3$  as precursor in the presence of HDA. The decomposition of the complex  $\text{Pt}_2(\text{dba})_3$  under  $\text{H}_2$  using a long alkylchain amine (HDA) in presence of SWCNTs leads to formation of stabilized Pt particles on SWCNTs with an average size of 2 – 3 nm. Scherrer's approximation cannot be used in dispersed nanoparticles because there is a widely deviation as was demonstrated.

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