



## Carbon nanotubes as support of well dispersed platinum nanoparticles via colloidal synthesis



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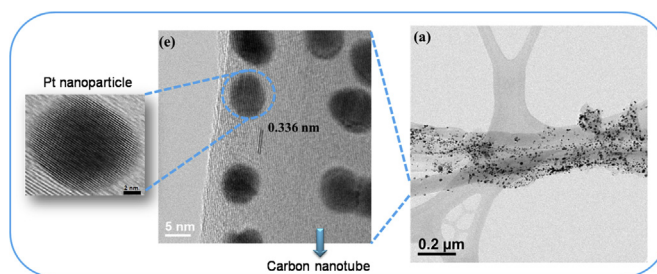
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### HIGHLIGHTS

- The Pt nanoparticles shows spherical shape with a good distribution.
- Pt colloidal nanoparticles were supported onto carbon nanotubes.
- The size of the Pt nanoparticles was between  $6.1 \pm 0.85$  and  $6.5 \pm 1.5$  nm.
- X-ray diffraction shows diffraction peaks corresponding to graphite and metallic Pt.
- Electrochemical activity of Pt/MWCNT was higher than the Pt/C.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Pt colloidal nanoparticles were synthesized by simultaneous chemical reduction of metallic salts in presence of poly (N-vinyl-2-pyrrolidone) as protecting agent. The uniform and highly ordered Pt colloidal nanoparticles were associated to well dispersed particles ranging in particle size distribution around  $4.5 \pm 1.9$  nm. The nanoparticles were deposited onto multiwalled carbon nanotubes (MWCNT). MWCNT were synthesized by chemical vapor deposition (CVD) method. Before the metal impregnation, the MWCNT were treated with  $\text{HNO}_3$  in reflux. Prepared Pt catalyst were characterized by various physical and electrochemical techniques, that is, X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Raman spectroscopy and cyclic voltammetry (CV). Raman spectroscopy reveals changes intensity ratio  $I_G/I_{G'}$  in the samples, after the cleaning process and Pt loading, indicating changes in the crystallinity of the materials. HRTEM showed Pt particles between  $6.1 \pm 0.9$  nm and  $6.5 \pm 1.5$  nm are well dispersed along the carbon nanotubes. XRD patterns show characteristics peaks corresponding to graphite and metallic Pt. The electrochemical properties of the MWCNT supported Pt nanoparticles were investigated by analyzing the response of the nanostructured catalyst for cyclic voltammetry and compared with a commercial material.

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### 1. Introduction

The synthesis of noble metal nanoparticles, particularly Pt, has been a growing field of interest in recent years. Due to their optimal physicochemical characteristics, these kinds of nanoparticles have been utilized in several technological applications such as catalysts, sensors, optical devices, etc. [1–3]. Good quality colloidal

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nanoparticles can be produced using different reactants, as well as reduction methodologies as thermal [4], photochemical [5], electrochemical [6] and chemical [7–9]. However, only some of these methods ensure the synthesis of materials with good control on the size and particle distribution. The chemical reduction method has advantages compared to others in the synthesis of metal nanoparticles. This method is simple and reproducible, and is possible to obtain homogeneous and nanometer scale particles (<10 nm) [10]. Furthermore, structure, shape and particle size can be controlled simply by varying the preparation conditions. The synthesis of nanoparticles with good dispersion is a first step to obtain nanomaterials with high catalytic activity in various electrochemical reactions. The next step would be support these colloidal dispersions on nanostructured carbon in order to obtain well-dispersed nanoparticles. The supporting material as well as the nanoparticles synthesis, have a direct influence to provide dispersion, stability and in consequence, a possible good electroactivity in the reactions of a fuel cell.

Platinum has attracted important attention because it is a stable and excellent catalyst for many purposes, such as its application in PEM fuel cells as cathode for the oxygen reduction reaction at relatively low temperature. It is well known that the Pt catalytic activity strongly depends on the particle shape, size and size distribution [11], as well as the support, which determines the degree of dispersion of the catalyst. It has been reported that the best electroactivity performance of Pt/C were obtained with particles in the range of 2–5 nm, and carbon particles in the range of 30–100 nm in diameter [12]. Pt nanostructured supporting material most commonly used is carbon black and activated carbons, with Vulcan XC-72 being the most representative. These conventional carbonous materials have been investigated in long time performance tests. It was found that carbon blacks get oxidized in a fuel cell environment, promoting the agglomeration of Pt and decreasing in consequence the electrocatalytic activity. Therefore, the catalysts durability is a critical issue to be resolved for the commercialization of the PEMFC [13]. Carbon nanotubes (CNTs) are attractive materials for catalyst support in PEMFC because of their morphology and interesting properties such as nanometric size, highly accessible surface area, excellent corrosion resistance, good electrical conductivity, and high stability, compared to conventional carbon black powders [14]. The deposition of Pt metal nanoparticles on CNTs has resulted in a higher catalytic activity compare to carbon black support [15,16]. However, the high dispersion of Pt nanoparticles with controlled loading is still a challenge due to the inert surfaces of CNTs [17]. The deposition of Pt over CNTs can be achieved via diverse procedures such as, chemical vapor deposition [18], microwave-assisted polyol process [19], electrodeposition method [20], chemical reduction [21], wet chemistry impregnation [22] and hydrothermal method [23] among others. This paper reports the colloidal synthesis of Pt nanoparticles by chemical reduction method in presence of poly(-vinylpyrrolidone) [24,25] and NaBH<sub>4</sub> [26,27]; and their support on MWCNTs synthesized by chemical vapor deposition (CVD). The structural and morphological properties as well as the electrochemical characterization of the materials are presented.

## 2. Experimental section

### 2.1. Multi-walled carbon nanotubes synthesis

The MWCNTs used as support were obtained by CVD method using Vycor tubing as substrate. The precursor solution was a mixture of catalyst (1.9 g ferrocene, 98% from Aldrich) and toluene (25 ml, 99.8% from J.T. Baker). Argon gas (99.998% purity) was used to carry the precursor mixture into the Vycor tubing placed inside a

tubular furnace at 1173 K. After the MWCNT synthesis, the system was allowed to cool down at room temperature. MWCNTs inside the Vycor tubing were mechanically removed. Acid treatment is a well-accepted process not only to clean MWCNTs but also to functionalizing them, incorporating carboxyl and hydroxide groups which improves the anchoring of Pt ions [17,28]. The MWCNTs were purified to remove residual iron and functionalized in a reflux system with 30% H<sub>2</sub>O<sub>2</sub> (30% from J.T. Baker) and HNO<sub>3</sub> (66.5% from J.T. Baker) by 2 h, and 24 h respectively at 373 K. Finally, the MWCNTs were washed several times with triple distilled water (from J.T. Baker).

### 2.2. Synthesis of MWCNT supported Pt nanoparticles

Colloidal dispersions of Pt nanoparticles were prepared as previously reported by the authors [10]; different amounts of platinum tetrachloride (99.99% from Aldrich) were dispersed in methanol (1.0 mmol dm<sup>-3</sup> and 5.1 mmol dm<sup>-3</sup>), then, 30 mg of poly (N-vinyl-2-pyrrolidone) (PVP, 99.9% from Aldrich) was added to 25 ml of the metal ion solution as the capping agent. A stable homogeneous dark brown colored colloidal dispersion was formed after adding 1 ml of a 0.044 mol dm<sup>-3</sup> solution of NaBH<sub>4</sub> (98.7% from Ferment).

Pt nanoparticles supported on MWCNTs were prepared as follows; 100 mg of MWCNTs were dispersed in methanol with strongly ultrasonication for about 1 h. Afterward, the Pt colloidal dispersion was added and vigorously stirred during 30 min. Two samples with different Pt loading were tried, with concentrations of 1.0 and 5.1 mmol dm<sup>-3</sup> for samples of 10 wt.% (Pt10) and 20 wt.% (Pt20), respectively. Then they were dried at around 393 K until the solution was completely evaporated. Finally, anchoring of Pt nanoparticles on the carbon nanotubes surface was carried out by a thermal process in a tubular furnace adapted with a quartz tube, where samples were annealed at 623 K under nitrogen atmosphere for 30 min with a flow rate of 50 ml min<sup>-1</sup>.

### 2.3. Characterization

The samples were characterized by X-Ray Diffraction (XRD) in a Panalytical Xpert system using Cu K $\alpha$  radiation at 40 kV and 30 mA, the scanning angle  $2\theta$  was varied between 20° and 80°, at 0.1° min<sup>-1</sup>.

High Resolution Scanning Electron Microscopy analyses (HRSEM) were performed with a field emission scanning electron microscope JEOL JSM-7401F operated at low voltage. To determine the catalysts compositions, energy dispersive X-ray spectroscopy analysis (EDS) was done with a Bruker detector attached to a Tescan Vega 3 scanning electron microscope with an operating voltage of 20 kV. High resolution transmission electron micrographs were obtained in a JEOL JEM-2200FS transmission electron microscope at 200 kV, in order to get information about the mean particle size and distribution of Pt on colloidal solution and Pt on MWCNTs, respectively. In order to get the nanomaterials structure, Raman spectroscopy measurements were carried out using a Horiba Jobin Yvon model LabRam HR VIS. In addition, thermogravimetric analyses were carried out in a TGA Q500 instrument, in air from room temperature to 1223 K using a heating ramp of 283 K min<sup>-1</sup>.

On the other hand, all electrochemical experiments were performed in a conventional three-electrode test cell at room temperature. An Ag/AgCl (saturated KCl) electrode and a platinum wire were used as reference and counter electrodes respectively, and 0.5 M H<sub>2</sub>SO<sub>4</sub> as electrolyte. The working electrode was a thin layer catalyst supported on a glassy carbon electrode. The previously polished working electrode had an area of approximately 0.071 cm<sup>2</sup>. The electrochemical active area of the sample was determined by cyclic voltammetry analyses using a BAS RDE-2 potentiostat/galvanostat instrument with a scan rate of 20 mV s<sup>-1</sup>.

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