

In-situ Pd–Pt nanoalloys growth in confined carbon spaces and their interactions with hydrogen



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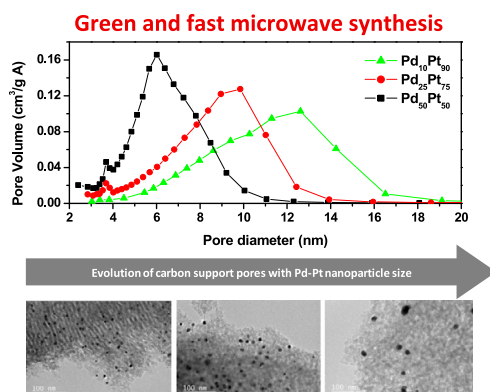
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HIGHLIGHTS

- C@Pd–Pt hybrids were prepared by a fast and green one-pot microwave method.
- Bulk immiscible Pd–Pt nanoalloys in the whole composition range were obtained.
- Pd–Pt composition has an important effect on the nanoparticle and carbon pore size.
- Nanoalloys size/shape can be tuned by several synthetic parameters.
- The hydrogen absorption strongly depend on the nanoalloy size and confinement.

GRAPHICAL ABSTRACT



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ABSTRACT

Optimized synthesis of Pd–Pt nanoalloys confined in mesoporous carbons by a simple and fast one-pot microwave assisted approach is reported herein. The influence of several synthetic parameters (Pd–Pt composition, cross-linker type, Pd precursor type and its addition time) on the carbon framework and Pd–Pt nanoparticles formation and characteristics was investigated. Small and uniform distributed nanoparticles on tailored mesoporous carbons are obtained in short time compared to the classical approaches. The metallic composition has a great influence on the nanoparticle size and an important effect on the carbon pore size distribution. When Pt content increases (from 10 to 90 at.%), an increase in the particle size (from 6.5 to 18 nm) and in the pore size distribution of the carbon support (from 3 to 13 nm) is observed. Bulk immiscible Pd–Pt alloys were formed in the whole composition range as highlighted by the linear relationship between the lattice parameter and the metal content. The Pd precursor, the cross-linker and the addition time proved to have a significant effect in the final size/shape of the Pd–Pt nanoparticles.

The optimized synthetic method can successfully tailor the size and the confinement of nanoparticles into the carbon matrix. Consequently, the hydrogen absorption properties and hydride formation can be tuned by the particle size for the richest Pd–composition nanoalloy (Pd₉₀Pt₁₀). The smaller Pd–Pt nanoparticles (6 to 20 nm) are confined in the carbon matrix and are surrounded by a graphitic layer preventing the hydrogen absorption while larger particles (50 nm) absorb hydrogen with metal hydride formation.

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1. Introduction

The nanoconfinement and downsizing of metal particle size become a very interesting approach to tailor the hydrogen uptake and to improve the absorption/desorption kinetics in comparison with bulk materials [1,2]. Among all the metals, Pd is considered to be unique material with a strong affinity to hydrogen, owing to both its catalytic and hydrogen absorbing properties [3]. Although it is known that downsizing the Pd size decreases the hydrogen absorption [4] less knowledge are available about the Pd-metal alloys size, composition or confinement effects on hydrogen absorption uptake and hydride formation. For most Pd-metal systems (Pd-Co, Pd-Ni, Pd-Rh) we studied [5–9] the hydrogen uptake decreases with the particle downsizing and the increase of the substitution metal amount in the alloy. For more than 25 at.% of metal substitution in Pd nanoparticles, hydrides are not formed anymore under standard temperature and pressure conditions. Both, Pd and Pt, have high electrocatalytic activity, due to their relatively high energy density and convenient form factor and are considered the most efficient noble-metal catalysts for direct alcohol fuel cells (DAFCs). For this reason Pd-Pt nanoparticles have been tested for DAFCs [10,11] and direct methanol fuel cells (DMFC) [12–14] showing better performance than single metal nanoparticles materials. In addition, Pd-Pt nanoparticles have been also tested as sensors [15,16].

Different approaches have been used for the preparation of supported Pd-Pt nanostructures, the most used method is the wet chemical reduction [12,14,16–21]. Other routes like electrochemical deposition [15], hydrogen absorption/desorption process [22], plasma discharge [10] and microwave radiation [23,24] have been used for the synthesis of Pd-Pt bimetallic particles. In all these works a carbon support already synthesized or a commercial available one is impregnated with a metallic salt solution followed by a reduction step to form the nanoparticles supported on carbon [11, 25,26]. Therefore, these multi-step synthesis routes can be highly time consuming and not environmental friendly. Chemical reduction allows preparing alloy and core-shell nanoparticles if the metal reduction occurs at the same time for both metals or if one metal is reduced before the other one, respectively. The most commonly used reducing agent is sodium borohydride (NaBH_4) [14,17, 21] (or KBH_4 [16]), a flammable, corrosive, toxic and health hazardous product, reasons why another safer and softer reducing agents have been studied such as ascorbic acid [12], hydrazine [18] or ascorbic acid [13] among others. In other cases the use of a reducing solvent, like ethylene glycol, and stabilizers were successfully employed [27–30]. On the other hand microwave radiation has been used as a fast and low temperature method providing small dispersed Pt, Pd or Pd-Pt nanoparticles supported on graphene or on mesoporous carbons [24,31,32]. This approach provides a rapid and homogeneous heating of the sample enhancing the reaction and facilitating the uniform nucleation of the sample as well as a shorter crystallization time, very short induction period and moreover it is energy efficient and environmental friendly [33].

In previous works we prepared bimetallic nanoalloys by impregnation of a carbon host with metal solutions followed by a reduction step [2], but a ulterior H_2 thermal treatment was required. An alternative to the above multi-step routes for the preparation of carbon/metal nanoparticle materials is the one-pot approach. The one-pot approach allows the simultaneous formation of the mesoporous carbonaceous matrix and *in-situ* growth of the nanoparticles with no specific reducing treatment needed; the carbon reduces the particles during the synthesis. Hard-template route involving the use of silica scaffolds which are infiltrated with carbon and metal precursors have been proposed for the preparation of metal nanoparticles decorated on

carbons [34,35]. However, it should be underlined the important drawbacks related to the long synthesis procedure and expensive nature of hard-templates along with their removal process using dangerous reagents such strong bases or acids.

Therefore, a more convenient and faster soft-template route involving the co-assembly of phenolic resins and metal salt precursors in the presence of organic templates attracted recently greater attention [36]. We extended the one-pot soft-template route for the synthesis of mesoporous carbon containing bimetallic nanoparticles, Pd-Co [5] and Ni-Co [37], by evaporation induce self-assembly (EISA) and phase separation approaches using green phenolic resins contrary to most of the works employing carcinogen phenol-formaldehyde resins. However, the synthesis time remains long, from one day to several days depending of the method, and a thermopolymerization step previous to the carbonization is required to stabilize the phenolic resin network [5, 37].

In this work we report the optimization of a one-pot microwave assisted synthesis where the carbon material and Pd-Pt alloy nanoparticles are prepared in one step.

This microwave proposed synthesis allows decreasing the synthesis time to 4 h compared to the classical approach and in addition no thermopolymerization step is required. Besides, the use of environmentally friendly reagents, low temperature and low microwave powers makes this approach simple and green.

As far as we know no works about the one-pot synthesis of Pd-Pt decorated carbon were reported. Despite the simple synthesis approach, the nanoalloy particle size and composition control simultaneously with the carbon framework mesostructure and formation is very challenging and not often addressed. The understanding of main factors affecting the *in-situ* growth of alloy NPs in confined spaces of a carbon and their impact on their final characteristics is worth of investigation. Different Pd-Pt compositions were synthesized to study the effect of the chemical composition on the properties of carbon and nanoparticles formation. A systematic study of the influence of several synthetic parameters on the morphology and structure of the C@PdPt hybrid materials was performed by combined TEM, EDX and XRD techniques while the textural properties were determined by nitrogen adsorption. The influence of particle size and confinement on the hydrogen absorption was measured by *in-situ* XRD. Mesoporous carbons with surface areas around $630 \text{ m}^2 \text{ g}^{-1}$ with homogeneously dispersed and confined Pd-Pt nanoparticles, with particle sizes between 6.3 and 50 nm, were obtained by tuning the experimental conditions. Despite some works attended to prepare different carbon supported Pd-Pt compositions none of them accomplished the preparation of the alloys in the whole range of composition [14,16,30]. Carbon supported bulk-immiscible Pd-Pt nanoalloys in the whole range of composition are reported for the first time. The hydrogen absorption is strongly affected by the nanoparticles confinement in the carbon network.

2. Experimental

2.1. Material synthesis

Mesoporous C@Pd-Pt hybrids were synthesized by one-pot microwave assisted method. A mixture of a triblock copolymer (Pluronic F127), phenolic resin (phloroglucinol-glyoxal or phloroglucinol-glyoxylic acid) and metallic salts were dissolved in ethanol/water and the reaction was induced using a CEM discover SP microwave synthesizer. The reaction was carried out under stirring in an open 100 mL flat-bottomed flask. Different cross-linkers and palladium precursors were used in order to study their influence on the particles size and dispersion.

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