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Palladium or palladium hydride nanoparticles synthesized by laser ablation of a bulk palladium target in liquids

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ABSTRACT

Laser ablation of a bulk Pd target in DIW, acetone or ethanol was carried out for the production of nanoparticles colloidal solutions. The size distribution of the nanoparticles follows log-normal function for all three liquids, with a median diameter of 3, 1.1 and 1.5 nm and standard deviation of 0.65, 1 and 1, respectively. Amorphous carbon is found on the nanoparticles synthesized in the hydrocarbons (acetone or ethanol). In DIW pure Pd nanoparticles were generated while ablation in acetone or ethanol lead to the synthesis of palladium hydride (PdH_x) nanoparticles. These nanoparticles can be used in hydrogen storage applications.

1. Introduction

Pd is a transition metal from the so-called platinum group metals with the lowest melting point and the lowest density from all of them. These elements have outstanding catalytic properties, high resistance to wear and tarnish, resistance to chemical attack, excellent high temperature characteristics and stable electrical properties which makes them to have a widespread use in different applications.

In particular, Pd nanoparticles are very important nanomaterials for utilization mainly as catalysts in different reactions such as conjugate reduction of unsaturated carbonyl compounds for the production of saturated alcohols [1], coupling reactions [2], hydrogenation reactions [3] and other types of organic reactions [4]. One very important application of Pd nanoparticles is in their use as hydrogen storage materials in for instance fuel cells, batteries and supercapacitors for the future production of "clean" energy [5]. This application of Pd nanoparticles is based on the characteristic property of the metal to be able to absorb large amounts of hydrogen as high as almost nine hundred times of its own volume and thus Pd is named as "the hydrogen sponge". In fact, solid state storage of hydrogen is the safest and most effective way of routinely handling hydrogen over the gas and liquid storage methods. Nanocrystalline Pd reacts to form palladium hydride (PdH_x) faster and at a lower temperature than bulk Pd and can be made to release hydrogen to regenerate Pd [6]. Nanoscale metal hydrides in general are known to have faster reaction kinetics of hydrogen uptake and release (due to the much larger available surface area), a lower desorption temperature and activation energies than their bulk analogues, and hydrogen contents which are size dependent.

Pd nanoparticles are traditionally synthesized by chemical, sonochemical, electrochemical, thermal or biological reduction of a palladium salt [7–9]. By using the method of laser ablation of the bulk target material in liquids, Pd nanoparticles have been first synthesized more than ten years ago [10], followed by more detailed investigations in recent years [11–14], in view of the main advantages of this method that no chemical precursors are needed for nanomaterials synthesis and that ultrapure colloidal solutions of nanoparticles can be produced. These studies report the feasibility of the method of laser ablation for the synthesis of Pd nanoparticles with desirable morphological and structural properties.

This paper involves the synthesis of Pd or PdH_x nanoparticles by laser ablation of a bulk Pd target in liquids. We demonstrate that laser ablation of a bulk Pd target in liquid can be used as a direct method for an in situ hydrogenation of the generated Pd nanoparticles (at the same time as their generation takes place) and thus as a method for the one-step synthesis of PdH_x nanoparticles. By choosing appropriately the liquid in which ablation takes place either Pd or PdH_x nanoparticles can be produced.

2. Experimental details

Laser ablation for nanoparticles generation was carried out with a picosecond (12 ps) pulsed laser source at beam wavelength of 532 nm using an average power of 2.6 or 1.6 W and a high pulse repetition rate of 200, 80 or 10 kHz (pulse energy of 8, 32.5 or

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260 μJ). The use of a high pulse repetition rate laser beam ensures a high throughput of ablation (a parameter defined as the product of the volume ablation rate, i.e. the volume which is removed per pulse, with the pulse repetition rate and essentially characterizes the volume of the material which is removed by the laser beam per unit time) at a relatively low peak fluence and therefore a high efficiency of ablation. The implication of this to the formed nanoparticles colloidal solution is that for the same fluence the use of a higher pulse repetition rate is expected to lead to the formation of a nanoparticles colloidal solution with a higher concentration for the same ablation time duration. The target was a bulk piece of Pd metal (fcc) (purity 99.999%) and ablation was carried out with the target lying at the bottom of a Pyrex petri-dish with diameter of 5 cm, filled each time with deionized water (DIW), acetone or ethanol, at a height of ~5 mm. The beam was scanned onto a stationary sample, in a circular spiral (diameter 3 mm, pitch 0.006 mm and scanning speed of 25 mm/s, 10 overscans) by using a computer controlled Scanning Galvo head (SGLV) and ablation was carried out for 8.4 min each time (1 ablation cycle), producing ≈0.7 mg of nanoparticles.

The nanoparticles colloidal solutions were characterized by UV–vis spectrophotometry (Jasco UV/Vis/NIR V-570). The synthesized nanoparticles, from solution droplets dried out onto carbon coated copper grids, were characterized in Scanning Transmission Electron Microscopy-Bright Field (STEM-BF) imaging mode in a FEI-Titan microscope operated at 200 kV and equipped with a Cs probe corrector and from droplets dried out onto clean glass substrates by X-ray Diffraction (XRD) using a diffractometer with a Cu Kα source (λ = 1.5406 Å) (Panalytical X'Pert Pro), Raman spectroscopy (pumping beam at λ = 543 nm) (Renishaw InVia Microscope) and X-ray Photoelectron Spectroscopy (XPS) using a spectrometer with Al Kα primary radiation (1486.6 eV) at a pass energy of 40 eV for high resolution scans and 160 eV for survey scans. Peak deconvolution of the XPS spectra was performed by using the software XPSPEAK4.1 using a standard procedure, first taking a background and then fitting using the minimum number of peaks to achieve a χ^2 value of <1.

3. Results and discussion

In the method of synthesis of metal nanoparticles by short pulse laser ablation of a bulk target material at low fluences, the largest percentage of the nanoparticles are formed by the nucleation in the vapor phase of the ablation plume species. This is because for most of the materials, the surface enthalpy of the material during laser ablation (at the present case estimated equal to $\sim 1.9 \times 10^9$ J/kg by taking into account the ablated mass of the material per ablation cycle of ≈0.7 mg and the pulse energy of 32.5 μJ) is by four orders of magnitude larger than its sublimation (and therefore its vaporization) enthalpy, which for Pd is equal to 3.76×10^5 J/mol [15]. However, at higher fluences due to the dissipation of laser energy into heat out of the initial volume in which the radiation is absorbed, a large percentage of the nanoparticles correspond to molten material which is emitted directly from the target as droplets. Plasma plume was seen to be formed above the target surface at the place of incidence of the laser beam onto the material surface, for all ablation conditions used.

TEM images of the nanoparticles are shown in Fig. 1a–c. It is seen that spherical, solid nanoparticles are obtained in all three liquids. Their size distribution histograms by counting approximately 500 particles in images of nanoparticle ensembles obtained on different areas on each grid are shown in Fig. 1d–f. The histograms are described quite well by log-normal functions with median diameters of $\langle d_0 \rangle$ = 3.3, 1.1 and 1.5 nm and standard deviations of σ = 0.65, 1 and 1, respectively. The smaller median diameter of

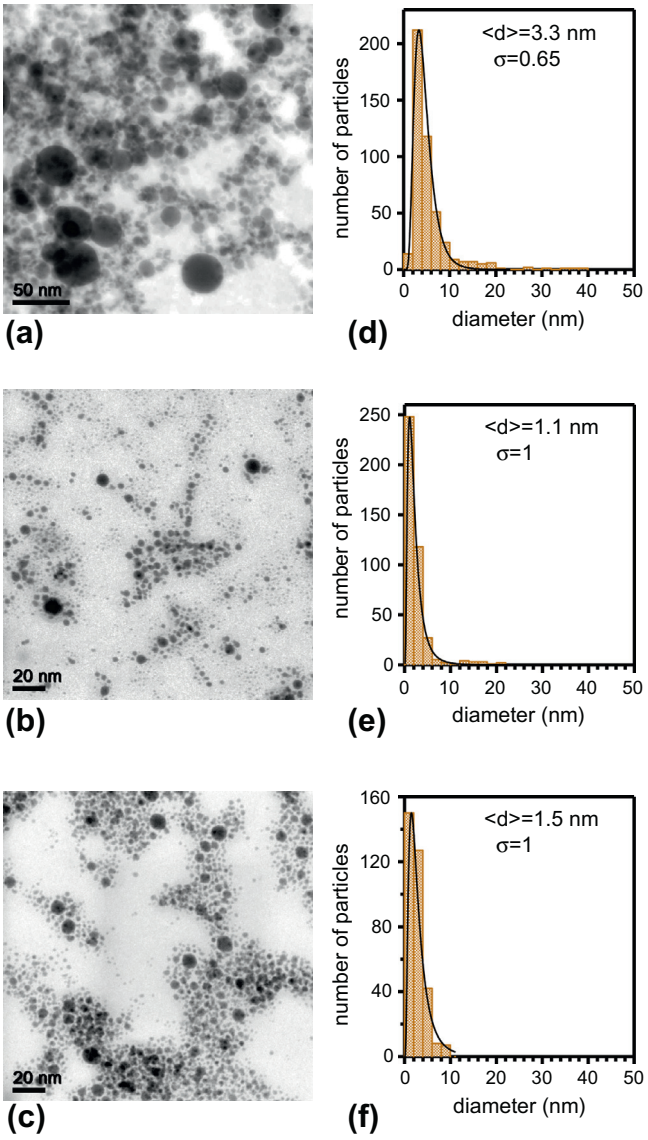

Fig. 1. TEM images and corresponding size distribution histograms of the nanoparticles synthesized in: DIW (a and d), acetone (b and e), and ethanol (c and f), respectively.

the nanoparticles obtained in acetone and ethanol as compared to the median diameter of the nanoparticles obtained in DIW can be understood by the formation of a carbon shell on the surfaces of the nanoparticles synthesized by the laser ablation in the hydrocarbons due to their pyrolysis by the laser beam – as it will also be supported by Raman measurements on the nanoparticles, presented later in the paper – which in turn results in the interruption of nucleation and hindering of the growth of embryonic nanoparticles, an explanation already suggested for similar observations in the case of Au nanoparticles synthesized by laser ablation also in hydrocarbons [16].

UV–vis absorption spectra measured from the nanoparticles colloidal solutions for nanoparticles synthesized in DIW and ethanol are shown in Fig. 2. All colloidal solutions were stable against sedimentation for at least several months with no addition of any surface-active substances. The absorption spectra from the solutions of nanoparticles are typical of nanoparticles of Pd synthesized by using other methods reported in the literature [17] and in agreement with calculations for nanoparticles in liquids performed using the Mie theory [18], where a broad continuous absorption in