



Preparation of small size palladium nanoparticles by picosecond laser ablation and control of metal concentration in the colloid



E. Giorgetti^{a,*}, P. Marsili^{a,b}, S. Cicchi^c, L. Lascialfari^{a,c}, M. Albiani^c, M. Severi^c, S. Caporali^{c,e}, M. Muniz-Miranda^c, A. Pistone^d, F. Giammanco^b

^a Istituto dei Sistemi Complessi, Consiglio Nazionale delle Ricerche, Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

^b Department of Physics “E. Fermi”, University of Pisa, Largo Bruno Pontecorvo 3, 56127 Pisa, Italy

^c Department of Chemistry “Ugo Schiff”, University of Firenze, Via della Lastruccia 3, 50019 Sesto Fiorentino (FI), Italy

^d Department of Electronic Engineering, Industrial Chemistry and Engineering, University of Messina, C.da di Dio, 98166 Messina, Italy

^e Consorzio INSTM, Via Giusti 9, 50123 Firenze, Italy

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ABSTRACT

We assessed a method for the preparation of small, highly stable and unprotected Pd nanoparticles by picosecond laser ablation in 2-propanol. The nanoparticles can be extracted from 2-propanol by centrifugation and redispersed in water, where a strongly negative ζ -potential assures long term stability. The proposed procedure permits reduction of particle size down to 1.6 nm and optimization of the Pd(0):Pd(II) ratio which, in the best cases, was of the order of 6:1. The increase of this ratio with ablation times has been correlated to the high temperature conversion of PdO to metallic Pd by a simple theoretical model. A study of the relationship between colloid absorption at 400 nm and Pd concentration permitted the role of PdO in the determination of the UV–vis spectra to be clarified and the limits of the Mie theory for the evaluation of colloid concentration to be established. The absorption at 400 nm can be used as a fast method to estimate the Pd content in the colloids, provided that a calibration of the ablation process is preliminarily performed.

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1. Introduction

Pd is widely used, as metal or in the form of its salts, to catalyze a number of synthetic processes [1,2]. In the form of nanoparticles (NPs), it is employed in sensors [3,4] and photoresponsive devices [5,6], as well as for the decoration of polymers [7] and carbon nanotubes for the development of novel heterogeneous catalysts [8]. The large surface to volume ratio exhibited by NPs is expected to greatly improve the catalytic activity [9,10]. NPs size also represents a key parameter in the development of nanohybrids that are based on PdNPs-decorated Multi Walled Carbon Nanotubes (MWCNTs) [11,12]. Preliminary results on the decoration of functionalized MWCNTs with AuNPs [13] suggested that NP size determines surface coverage of the nanotubes, as small NPs are the most efficient.

In addition to the size of the nanostructures, catalytic processes strongly depend on the efficient interaction between catalyst and environment, so that surface cleanliness is expected to play a major role. In this regard, Pulsed Laser Ablation in Liquid (PLAL) seems to be a promising procedure for the preparation of NPs because, unlike

current wet chemical methods, it permits the synthesis of stable metal colloids also in pure solvents and, under proper fabrication conditions, with no need of stabilizing agents [14].

With respect to the most studied metals, such as Au and Ag [14], only a limited number of papers is available in the literature which describe PLAL of Pd. Most of them use the fundamental wavelength or the second harmonic of Q-switched Nd:YAG lasers, namely 1064 or 532 nm, and nanosecond (ns) pulses [15–22], and different liquids, such as deionized water (DIW) [15,16,18,19,21–24], acetone [17,20,23–25] or other organic solvents [20,24]. For such preparation conditions [15–25], which mostly involve high laser fluences on target (namely from 1 up to 40 J/cm²), the PdNPs obtained by PLAL appear strongly polydisperse and relatively big, with average size ranging from 5 to 15–20 nm, which seem to increase with increasing laser fluence [19,20]. For example, in the case of DIW [15,18,19,22,23], the NPs size is always well above 5 nm, with large statistical distribution and strong evidence of coalescence, although ζ -potential and long term stability tests of the colloids were not reported. Examples of small PdNPs are described in Ref. [24], where 12 picosecond (ps) ablation of Pd at 532 nm and high repetition rate (10–220 kHz) is reported in DIW, acetone and ethanol, the smallest NPs being those obtained in ethanol.

* Corresponding author.

E-mail address: emilia.giorgetti@fi.isc.cnr.it (E. Giorgetti).

A major problem when performing the ablation of Pd, particularly in the case of DIW, is surface oxidation, which can be difficult to control and depends on several parameters, among which pulse duration and laser wavelength, as reported in Ref. [18]. In particular, XPS tests performed on PdNPs obtained in DIW with ns pulses and 1064 nm, permitted observation of both Pd(II) and Pd(IV) [18]. A considerable reduction of surface oxidation with respect to DIW is expected when performing the ablation in organic solvents, as observed in Ref. [23], which compares results obtained with DIW and acetone. However, the use of organic solvents under PLAL conditions was observed to strongly promote solvent decomposition and subsequent formation of amorphous carbon, which can passivate the surface of NPs. This phenomenon has already been detected by means of Raman or XPS spectroscopy in the case of Au [26] and Pd [20,23,24] NPs prepared by PLAL in acetone and ethanol.

The considerations discussed above suggest that it is important to find a convenient trade-off between the requirements of small size, stability and surface cleanliness, in order to synthesize PdNPs with interesting potentialities for catalytic applications. Therefore, this paper is aimed at establishing a method for the preparation of stable colloidal suspensions of small (mean diameter < 5 nm) and unprotected PdNPs by PLAL, in view of integration with the above mentioned applications and, particularly, with novel heterogeneous catalysts. For this purpose, we analyzed PdNPs obtained in 2-propanol under “gentle” ablation regime with the second harmonic wavelength of a ps Nd:YAG laser. We call our regime “gentle” since in our experimental conditions (fluences below 1 J/cm², ps pulses and low repetition rate) NP formation occurs in the absence of any phenomena related to shock wave formation, cavitation bubbles or bright plasma emission [27], generally, but only qualitatively claimed as responsible for particle growth [18]. We carried out a characterization of the colloids by UV–vis, Raman, XRD and XPS spectroscopy and TEM and HRTEM imaging. Moreover, as the concentration is an essential parameter to evaluate the activity of a catalyst, we also compared UV–vis experimental data and their theoretical modeling by the Mie theory, with direct Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES) concentration measurements, in order to verify the existence of a simple relation between absorbance at a fixed wavelength and Pd concentration.

2. Materials and methods

We prepared PdNPs by laser ablation of a Pd target with the fundamental wavelength or the second harmonic of a mode-locked Nd:YAG laser (EKSPLA PL2143A: rep. rate 10 Hz, pulse width 25 ps at 1064 nm and 18 ps at 532 nm). The experimental set up is described in detail in Ref. [26]. We performed the ablation in doubly DIW (18.2 M Ω cm @ 25 °C), acetone or 2-propanol. Acetone and 2-propanol, of 99.9% purity (Chromasolv[®] for HPLC grade) were purchased from Aldrich and used as received. The Pd target was supplied by Aldrich (0.5 mm thick, 99.9% purity).

Off-line UV–vis spectra were recorded with a Varian Cary 4000 using a 1 mm or 1 cm path-length quartz cell.

The ζ -potential of the colloids in water was measured with a Zetasizer Nano ZS90, Malvern Instruments.

Samples of PdNPs for Transmission Electron Microscopy (TEM) inspection were obtained by dropping a small amount of colloid onto carbon-coated copper grids, followed by evaporation. Low resolution images were recorded with a Philips CM12, 120 kV and High Resolution TEM (HRTEM) images were obtained with a Jeol JEM 2010 HRTEM operating at 200 kV. Particle mean diameter and dispersivity were determined by fitting the measured statistical distributions with a lognormal function.

X-ray Powder Diffraction (XRD) data were collected with a Bruker New D8 Advance diffractometer using Cu K α radiation. The Pd colloid was deposited on a silicon single crystal and

scanned over the 2θ range from 26° to 60° using a 0.02° step for 3 s on every step (total acquisition time 90 min). No filter was employed and the diffracted X-rays were collected using a Lynxeye_Xe detector.

X-ray Photoelectron Spectroscopy (XPS) experiments were carried out in an ultrahigh vacuum (UHV, 10^{−9} mbar) system equipped with a VSW HAC 500 hemispherical electron-energy analyzer using a non-monochromatic Mg K α X-ray source (1253.6 eV; anode operating at 10 kV and 10 mA). The spectra were collected in the constant-pass-energy mode ($E_{\text{pas}} = 44$ eV). The overall energy resolution was 1.2 eV. The binding energies were calibrated on the basis of the aliphatic C 1s peak at 284.8 eV. Samples for XPS measurements were prepared by drop-casting a small quantity of the colloid onto a glass slide and leaving it to dry at room temperature. Prior to the elemental scans, a survey scan was measured for all the samples in order to detect all the elements present. The spectra were deconvoluted by using XPS Peak 4.1 program with a Gaussian–Lorentzian mix function and Shirley background subtraction.

Raman spectra were measured using a Renishaw RM2000 microRaman apparatus, equipped with an Ar⁺ laser emitting at 514.5 nm. Sample irradiation was accomplished by using the 50 \times microscope objective of a Leica Microscope DMLM. The backscattered Raman signal was filtered by a double holographic Notch filter system and detected by an air-cooled CCD. All spectra were calibrated with respect to a silicon wafer at 520 cm^{−1}.

The determination of the Pd concentration in the samples was performed in triplicate by a Varian 720-ES Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES). 50 μ L of each sample were diluted to 5 mL with 0.1% suprapure nitric acid obtained by sub-boiling distillation, spiked with 0.5 ppm of Ge, used as an internal standard, and analyzed. Calibration standards were prepared by gravimetric serial dilution from commercial stock standard solutions of Pd at 1000 mg/L. Wavelengths used for Pd determination were 324.270, 340.458, 342.122 and 360.955 nm, whereas for Ge the line at 209.426 nm was used. The operating conditions were optimized to obtain maximum signal intensity, and between each sample, a rinse solution constituted by 2% v/v HNO₃ was used.

3. Results and discussion

Initially, we prepared PdNPs in DIW, with 1064 nm and a fluence on target of 0.5 J/cm². As reported in the [Supporting information \(SI1 and SI2\)](#), HRTEM inspection, UV–vis and XPS spectroscopy confirmed the expected presence of PdO, while the NP size was larger (7 nm) than our desired goal. Furthermore, these colloids exhibit a strong tendency to coalesce and they collapse in a few days after fabrication. According to recent literature, acetone permits the synthesis of very stable, small and quasi monodispersed AuNPs, when the ablation is carried out using a wavelength of 532 nm [26] while, in the case of PdNPs, it permits considerable reduction of surface oxidation with respect to water [23,24] and also the production of small size NPs [24]. However, in spite of their excellent stability (two years shelf life with no detectable sign of spectral changes) and considerable reduction of size (5 nm) and oxide contribution with respect to DIW, the NPs that we obtained in acetone are embedded in an abundant glassy matrix, which is likely composed of amorphous carbon, originating from solvent decomposition during the ablation (as described in the [Supporting information, SI3](#)). Therefore, we maintained short laser wavelengths and the low fluence, but changed to a different and scarcely studied solvent, namely 2-propanol [20], with the aim of finding the best compromise among NP size, colloid stability and surface contamination from Pd oxides or carbon. [Fig. 1](#) shows typical TEM micrographs of PdNPs obtained in 2-propanol using 532 nm radiation and

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