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Palladium nanoparticles produced by CW and pulsed laser ablation in water

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ABSTRACT

Palladium nanoparticles are receiving important interest due to its application as catalyst. In this work Pd nanoparticles have been obtained by ablating a Pd target submerged in de-ionized using both, pulsed as well as continuous wave (CW) laser. The influence of laser parameters involved in the formation in nanoparticles has been studied. Crystalline phases, morphology and optical properties of the obtained colloidal nanoparticles were characterized by means of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and UV/vis absorption spectroscopy. The obtained colloidal suspensions consisted of pure Pd nanoparticles showing spherical shape with diameters ranging from few nanometers to 5–60 nm. The moderate irradiance delivered by the CW laser favours high production of uniform nanoparticles.

1. Introduction

There's an increase interest in metal nanoparticles because of their unique physical and chemical properties related to the size effect when compared to bulk material. Due to their special properties, palladium nanoparticles play an important role in many industrial applications, such as, catalytic for organic reactions and in the reduction of automobile pollutants [1–3]. Their special sensitivity to absorb hydrogen make them good candidate as gas sensor and as hydrogen storage materials, in fuel cells or batteries [4–6]. For these applications it is important to synthesize nanoparticles with the adequate size distribution, morphology and crystallinity. There are different techniques for producing Pd nanoparticles, chemical, electrochemical, sonochemical, etc. [7–10]. Many of these techniques of production use precursors and solvents, or imply chemical reactions which can contaminate the obtained nanoparticles. Laser ablation of solids in liquids (LASL) enables obtaining nanoparticles with no need of chemical precursors. Its simplicity together with the advantage of producing nanoparticles with small size, narrow distribution and weak agglomeration make it suitable for metal nanoparticle fabrication. Pd nanoparticles have already been obtained by the LASL method using pulsed lasers, especially nanosecond and femtosecond lasers [11–13]. However nanoparticles can be synthesized in aqueous medium not only by the use of pulsed laser but also using a CW laser. In previous works we have used CW laser delivering moderate irradiance to produce TiO_2 nanoparticles in liquids [14,15]. In the present work we report the synthesis of Pd nanoparticles using a pulsed laser as well as a CW one. The results are discussed and compared.

2. Experimental

Plates of Pd with 99.99% of purity were cleaned and sonicated to be ablated by laser in water. The targets were attached to a bottom of a glass vessel and filled with distilled water up to 1 mm over the upper surface of the Pd plate. The first system used was a pulsed Nd:YAG laser with a wavelength of 1069 nm and delivering a maximum average power of 500 W. The laser beam was coupled to an optical fiber of 400 μm core diameter and focused onto the upper surface of the target by means of 125 mm of focal length lens, where the spot diameter at normal incidence for a pulsed laser was about 0.20 mm. Other parameters were varied as follows: laser pulse width 1–2 ms, frequency = 10 Hz, and pulse energy 2–8 J. The second laser source system was a CW monomode Ytterbium doped fiber laser (YDFL), with a maximum average power of 200 W and wavelength of 1075 nm. The delivered irradiance ranged between 2×10^5 and 10^6 W/cm^2. The laser beam was coupled to an optical fiber of 50 μm core diameter and focused on the upper surface of the target by means of by means of 125 mm of focal length lens. The laser beam was kept in relative movement with respect to the metallic plate at a scanning speed of 5 mm/s. After each experiment with both lasers, the obtained colloidal

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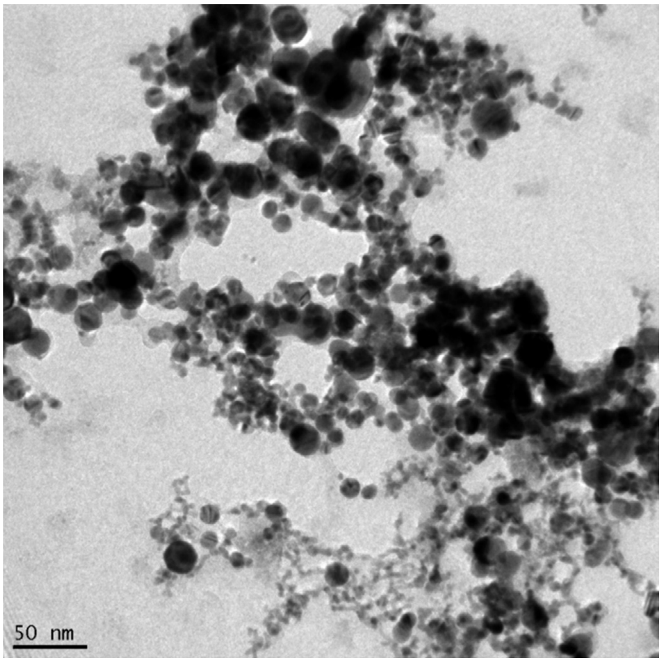

Fig. 1. Pd nanoparticles obtained by laser ablation of Pd plate in water using a pulsed Nd:YAG laser. f = 10 Hz, PW = 2 ms, PE = 2.4 J.

suspensions were dropped on carbon coated copper microgrids and on Si substrates for examination of particle morphology and microstructure. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL-JEM 2010 FEG transmission electron microscope equipped with a slow digital camera scan, using an accelerating voltage of 200 kV, to reveal their crystallinity and morphology. Identification of phases was achieved by comparing the diffraction patterns and distances from SAED of samples with ICDD (JCPDS) standards. The UV–vis absorption spectra of the colloidal suspension were measured in a Hewlett Packard HP 8452 A spectrophotometer.

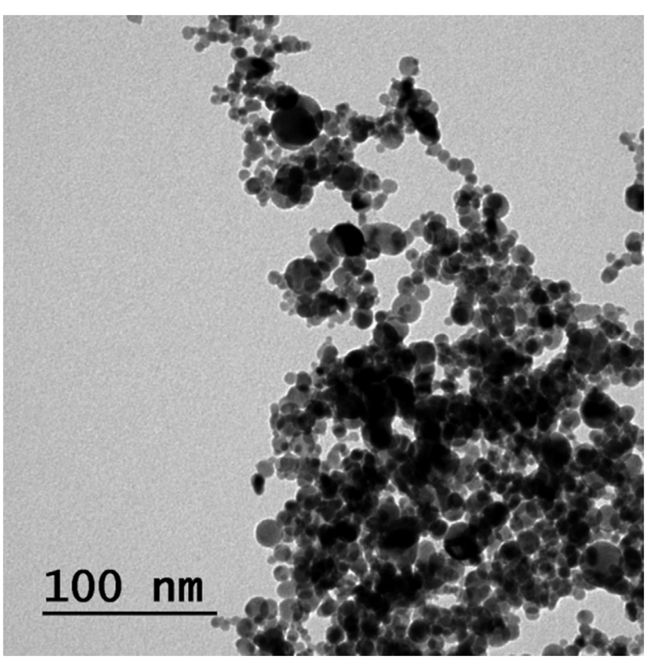

Fig. 2. Pd nanoparticles obtained by laser ablation of Pd plate in water using a CW Yb:YAG fiber laser. Average power = 200 W, scanning speed = 5 mm/s.

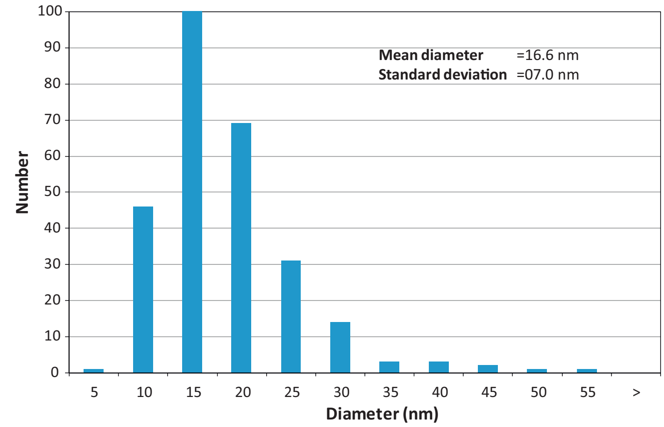

Fig. 3. Histogram of more than 300 particles obtained by laser ablation of Pd in water using a pulsed Nd:YAG laser. Mean diameter = 16.6 nm.

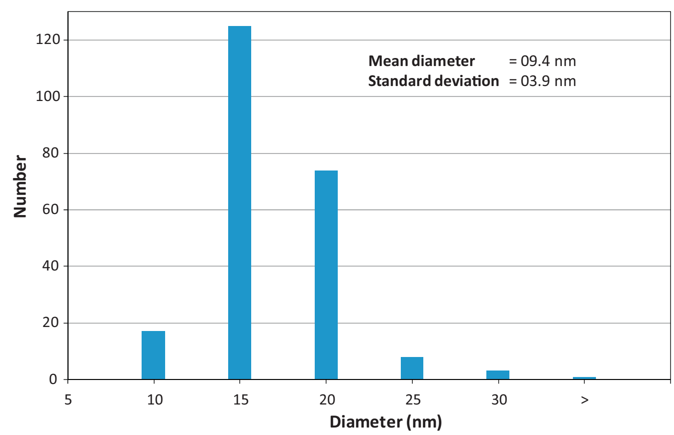

Fig. 4. Histogram of more than 300 particles obtained by laser ablation of Pd in water using a CW Yb:YAG fiber laser. Mean diameter = 09.4 nm.

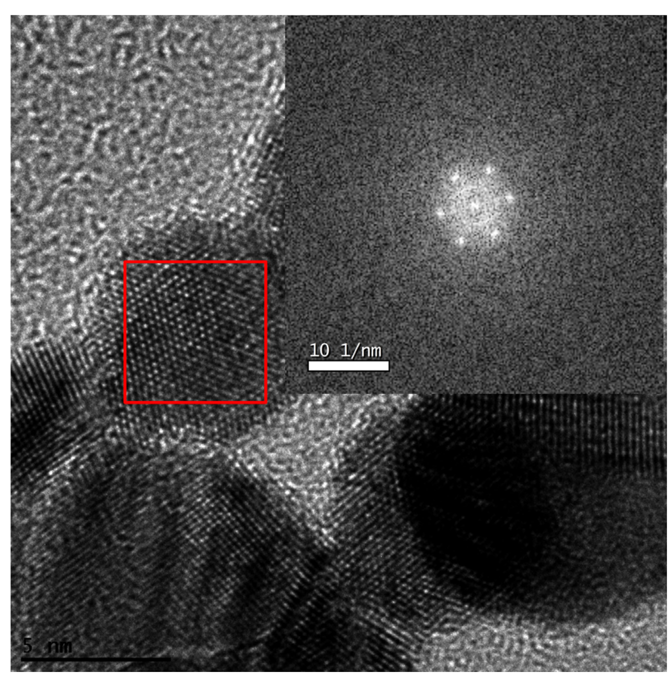

Fig. 5. HRTEM image of a group of Pd crystalline nanoparticles obtained by laser ablation in water using a pulsed Nd:YAG laser and FFT of the marked zone (inset).