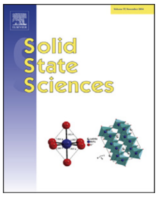
Solid State Sciences 37 (2014) 96–102

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie



The influence of laser wavelength and fluence on palladium nanoparticles produced by pulsed laser ablation in deionized water

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ARTICLE INFO

Article history:
Received 29 August 2014
Received in revised form
11 September 2014
Accepted 13 September 2014
Available online 16 September 2014

Keywords:
Palladium nanoparticles
Laser ablation in liquid
FETEM
Laser wavelength
Laser fluence

ABSTRACT

Homogeneous spherical palladium (Pd) nanoparticles were synthesized by pulsed laser ablation of a solid Pd foil target submerged in deionized water, without the addition of any external chemical surfactant. The influence of laser wavelength (355, 532, and 1064 nm) and fluence (8.92, 12.74, and 19.90 J/cm^2) on nucleation, growth, and aggregation of Pd nanoparticles were systematically studied. Microstructural and optical properties of the obtained nanoparticles were studied by field emission transmission electron microscopy (FETEM), energy dispersive X-ray spectroscopy, and UV–vis spectroscopy. FETEM micrographs indicate that the average nanocrystallite sizes are relatively low (3–6 nm) and homogeneous for the particles synthesized at the laser wavelengths of 355 and 532 nm. However, at a laser wavelength of 1064 nm, the average nanocrystallite size is relatively large and inhomogeneous in nature. Moreover, we observe that the mean diameter and production rate of particles increases with an increase in laser fluence. The selected area electron diffraction patterns obtained from isolated Pd nanoparticles show the characteristic diffused electron diffraction rings of polycrystalline materials with a face-centered cubic structure. Absorbance spectrum of the synthesized nanoparticle solution shows a broad absorption band, which corresponds to a typical inter-band transition of a metallic system, indicating the production of pure palladium nanoparticles. The present work provides new insights into the effect of laser wavelength and fluence on the control of size and aggregation of palladium nanoparticles in the liquid medium.

1. Introduction

Nanomaterials are currently at the cutting edge of fundamental materials research and are gradually finding application in our daily life. Nanomaterials can be defined as materials that have at least one dimension in an atomic or submicron scale (<100 nm) in contrast to their bulk counterparts [1]. The past two decades have witnessed an exponential, worldwide growth of activities in the field of nanoscale materials. This growth is driven by academic excitement surrounding new scientific phenomena and the potential hope for wider technological application [2]. Nanomaterials have a relatively larger surface area when compared to the same volume or mass of the material produced in a bulk form. It is known that when a given volume of material is divided into smaller pieces, the surface area increases. Thus, with a decrease in the size of a system, a greater proportion of atoms are found at its surface. Hence, nanostructured materials have a greater surface area per given volume compared to their bulk counterparts. However, the extent of surface area also depends on the shape of the material. Therefore, in nanoscience, we can conclude that both size and shape play an important role in determining the various properties of a synthesized product [3].

Compared to their bulk counterparts, monodisperse metal nanoparticles have attracted great attention due to their unique properties [4]. Metal nanoparticles with sizes smaller than the bulk excitonic length become important due to their demonstration of enhanced surface and quantum size effects that result in novel optical and electronic properties, which find potential technological applications [5]. Among all the metal nanoparticles, Pd nanoparticles are widely used as industrial and automotive catalysts because of their significant advantages in terms of activity, selectivity, lifetime, and reusability in heterogeneous catalysis [6]. However, the positive or negative effect of Pd nanoparticles on photocatalytic activity depends on various parameters such as particle size, morphology, and homogeneous dispersion of Pd on the targeted host matrices. Furthermore, as the number and size of the Pd nanoparticles increases (high amount of Pd loading), metal

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http://dx.doi.org/10.1016/j.solidstatesciences.2014.09.005
1293-2558/

nanoparticles act as recombination centers and hinder the photocatalytic efficiency [7]. Therefore, for efficient utilization of Pd nanoparticles for catalytic activity, an optimized size, shape, and structural homogeneity is highly preferred. In this light, recently, several experimental techniques such as sol–gel [8], hydrothermal [9], electro spinning [10], chemical vapor deposition [11], green synthesis [12], photochemical reduction [13], pulsed laser ablation [14], and spin coating [15] have been employed for synthesizing such specifically tailored Pd nanoparticles. Among them, the laser ablation in liquid technique is one of the most promising techniques. In comparison to colloidal chemical synthesis, the use of colloidal solutions for laser ablation in liquids is a relatively new technique. Intensive investigation on this technique was initiated only in the early 2000s [16]. Compared to conventional chemical synthesis, nanoparticles produced by laser ablation in liquid have greater advantages such as the high purity, good control of size, high crystallinity, easier to maintain stoichiometry, homogeneous size, inexpensive and accessible raw materials, capability of large scale production in short time, and the possibility of obtaining nanocomposites/doped systems by a single step modification. Moreover, the experimental setup is simple and inexpensive, and there is no need of sophisticated instrumentation/equipment such as high vacuum chambers [16,17].

In laser ablation in liquid synthesis, the particle size and morphology mainly depend on several experimental parameters such as the type of solvent, the existence of surfactant molecules, laser fluence, laser wavelength, and laser ablation times [18,19]. Considering all the synthesis parameters, a few recent reports are available on Pd nanoparticle synthesis by laser ablation in liquid. For instance, Cristoforetti et al. studied pulsed laser ablation of Pd in different organic solvents (acetone, 2-propanol, ethanol, toluene, and n-hexane) and also fabricated Pd nanoparticles in water with and without the sodium dodecyl sulfate surfactant [14,19]. Nishi et al. reported the properties of Pd nanoparticles ablated in heavy water and light water; the yield and average size of the nanoparticles have been discussed in relation to these properties [20]. Teppei et al. proposed a novel route to produce single-sized Pd nanoparticles with a narrow size distribution at the air-suspension interface by laser ablation [21]. Bonis et al. studied the dynamics of multiple cavitation bubbles produced by femtosecond laser ablation of a Pd target submerged in acetone by means of time-resolved fast shadowgraph technique and noticed that the size distribution of the laser-induced nanoparticles is strictly related to the cavitation bubble dynamics [22]. Boutinguiza et al. synthesized Pd nanoparticles by ablating a Pd target submerged in deionized water using both pulsed as well as continuous wave laser and studied the influence of laser parameters involved in the formation of these nanoparticles [23]. Karakhanov et al. proposed a new pulsed laser ablation–deposition technique in inhomogeneous electrical and electromagnetic fields, which was used to synthesize supported Pd catalysts and obtain Pd nanoparticles within the size range of 2–5 nm by varying the deposition conditions [24]. Among many experimental factors, it is vital to study the effects of laser wavelength and fluence because of their ability to exert great influence on the morphology, nanoparticle size, and production rate of Pd nanoparticles. So far, to the best of our knowledge, investigations on influence of laser wavelength and fluence on the production of Pd nanoparticles by pulsed laser ablation in deionized water without surfactant have not yet been reported. Motivated by the lack of research reports in this area, we have undertaken the present investigation and believe that this study along with earlier reports will be helpful for the production of monodisperse Pd nanoparticles with a narrow size distribution.

2. Materials and methods

Pd nanoparticles were synthesized by laser ablation in liquid of pure Pd foil (Sigma–Aldrich, purity: 99.9%, thickness: 0.5 mm) without any surfactant in deionized (DI)-water. The schematic diagram of the experimental setup for pulsed laser ablation in liquid is shown in Fig. 1. At first, the Pd foil was washed with ethanol and DI water using an ultrasonic cleaner to remove organic compounds, and it was fixed in a glass beaker containing 5 mL DI water. The level of DI water was around 10 mm above the target. Then, the beaker was installed on a turntable to avoid damage to the laser beam. The target was irradiated for 10 min at room temperature by a Nd:YAG laser with a repetition rate of 10 Hz and a pulse duration of 3–6 ns. The Nd:YAG laser beam was focused onto the Pd target by using a lens of 250 mm focal length. The final laser beam diameters on the surface of the target were adjusted to 0.8 and 1 mm. Three different wavelengths (355, 532, and 1064 nm) and two different pulsed energies (70 mJ – 1 mm diameter, 100 mJ – 0.8 and 1.0 mm diameters) were used for laser ablation. Therefore, the final laser fluences at the target surface were 8.92, 12.74, and 19.90 J/cm^2.

The microstructure properties of the as-synthesized Pd nanoparticles were investigated by using a field emission transmission electron microscope (JEOL JEM-2100F, Japan) with a Gatan 994 US 1000XP+ CCD camera working at 200 kV. Chemical analysis was carried out using a JEM-2100F FETEM equipped with an energy dispersive X-ray spectrometer (EDS, OXFORD X-MAX, UK) and a Silicon Drift Detector with an active area of 80 mm^2. The absorption of the obtained solution was measured using a UV–vis spectrophotometer (Shimadzu UV-1650 PC, Japan) in the wavelength range of 190–800 nm in a 10 mm quartz cell.

3. Results and discussion

The morphology, size, and crystal structure of Pd nanoparticles has been investigated using field emission transmission electron microscopy (FETEM). Fig. 2 shows typical FETEM images at different laser wavelengths with the same laser fluence (8.92 J/cm^2). The FETEM images in Fig. 2 demonstrate that both the size and the size distribution of the particles significantly depend on laser wavelength. The nanoparticles produced at wavelengths of 355 and 532 nm, show small sizes and uniformity. The formation of small-sized nanoparticles at these wavelengths can be explained as follows. When the laser irradiates on the Pd target surface, its energy will be absorbed leading to surface melting, vaporization, and

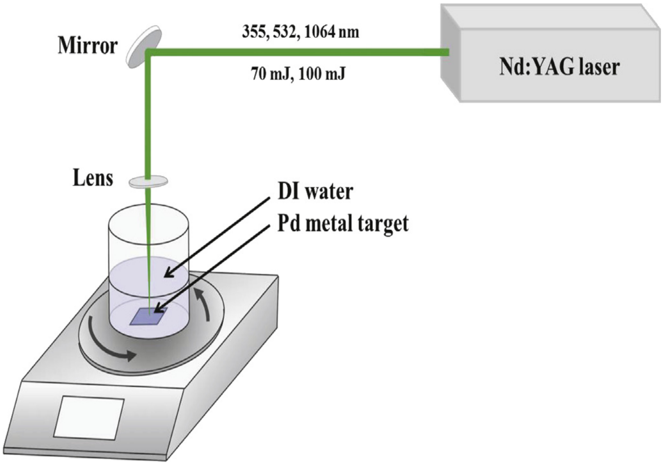

Fig. 1. The schematic diagram of the experimental setup for pulsed laser ablation in liquid.