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Dramatic changes of optical nonlinearity and ultrafast dynamics of palladium nanoparticles caused by hydriding

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ABSTRACT

Pd nanoparticles are deposited on one surface of a quartz sheet. Their optical nonlinearity and ultrafast dynamics in air and in hydrogen environment are investigated. The Pd nanoparticles exhibit self focusing and saturable absorption in air. In hydrogen environment with increasing hydrogen, the NPs maintain self focusing, however their nonlinear refraction index increases; and their nonlinear absorption changes from saturable absorption to reverse saturable absorption. In hydrogen environment, the acoustic breathing movement of these NPs damps more obviously and the contact between the NPs and quartz sheet is looser, comparing to that in air.

1. Introduction

In an environment with a low concentration of hydrogen, Pd dissolves hydrogen to form solid solution; with the increase of hydrogen, Pd changes into Pd hydride [1]. The hydriding of Pd causes the change of its physical properties [2], which is the basis of hydrogen sensing when the relationship between the change and the concentration is found. Recently, the linear optical and electric properties of Pd nanoparticles (NPs) in hydrogen environment have been reported, which bring about novel hydrogen sensing technologies [3–5]. Obviously, with hydriding, the property changes of Pd NPs are important issues to be investigated, in which the optical nonlinearity and ultrafast dynamic changes are important fields.

The reverse saturable absorption (RSA) of Pd NPs is reported [6–8]. And it is also reported that the nonlinear absorption (NLA) of Pd NPs changes from saturable absorption (SA) to RSA with the increasing intensity [9]. For the ultrafast dynamic of metal NPs, typically, under the irradiation of laser pulse, the electrons are excited and collide with the unexcited electrons, which leads to the thermalization of the electron gas. Subsequently the thermalized electron gas interacts with the lattice of the nanoparticle, leading to the thermalization of the nanoparticle. Finally the nanoparticle interacts with the solvent (or substrate) through the phonon–phonon interaction, which heats the solvent by consuming the thermal energy of particle [10]. Particularly, the ultrafast heating of lattice leads to the expansion of NPs, which subsequently undergoes radial contractions and expansions. This is the acoustic breathing movement which damps and decays as the NPs cools down by transferring its energy to the solvent [11]. Note that the optical nonlinearity and ultrafast dynamic of Pd NPs in hydrogen environment have not been reported.

Herein we investigate the optical nonlinearity and ultrafast dynamic of Pd NPs in air and in hydrogen environment. The Pd NPs exhibit self focusing (SF) and SA in air. In hydrogen environment, with the increase of hydrogen, the SF of the NPs enhances; and the NLA of the NPs changes from SA to RSA. The NPs experience acoustic breathing movement after the excitation of femtosecond laser, which damps obviously in hydrogen environment. The contact between the NPs and the quartz sheet is looser in hydrogen environment. The underlying mechanisms of the optical nonlinearity and ultrafast dynamic are explained.

2. Experimental details

The Pd NPs are deposited on one surface of a quartz sheet (1 mm thickness) by means of low energy cluster beam deposition method. Details of this method can be found elsewhere [5,12]. A copper grid with an amorphous carbon film is stuck on the quartz sheet to accept the Pd NPs, and is used to perform the TEM characterization. The deposition time of the NPs is 60 min (only one sample is fabricated). The morphology and crystalline structure of the Pd NPs are

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characterized by using a TEM (TECNAI F20s). The optical extinction spectrum of the Pd NPs are acquired by using a spectrophotometer (UV-1800).

The optical nonlinearity and ultrafast dynamic of the NPs are investigated by using the Z-scan and pump-probe technique, respectively. A laser system emits pulse of 800 nm (120 fs, 100 Hz) is used to perform the Z-scan experiment. There is another laser system which includes a regenerative amplifier and an optical parametric amplifier (OPA). The pulses of 515 nm (120 fs, 20 Hz) emitted by the OPA are also used to perform the Z-scan experiment. And the pulses emitted by the regenerative amplifier are frequency-doubled to 515 nm (120 fs, 20 Hz), which are used to perform the pump-probe experiment. In the Z-scan experiment, each laser beam is focused by a 20 cm focal length lens. The radius of each beam at the focus is 30 μm. The diffraction length of the focused beam at 800 and 515 nm is 3.53 and 5.49 mm, respectively. The thickness of the sample (1 mm) is smaller than the diffraction lengths, satisfying the demand of thin sample in the Z-scan technique. A closed chamber with two parallel glass windows (1 mm thickness) at its left and right wall is used. At the center of the chamber the sample is placed parallelly to the windows. In the Z-scan experiment, the beam irradiates the windows and sample vertically from $-z$ to $+z$ direction (i.e. from left to right). The dimension of the chamber along the beam is 10 cm. For a Z-scan of the sample from −3 (or −2) to 3 (or 2) cm, the left window is moved from −8 (or −7) to −2 (or −3) cm, and the right window is moved from 2 (or 3) to 8 (or 7) cm. Namely, neither the left nor the right window is moved very close to or pass the focus of the laser beam. So the nonlinearity of glass does not exhibit. In the pump-probe experiment the probe beam irradiates the windows and sample vertically. An inlet and outlet pipe connects the chamber, through which the hydrogen and mixed gas can be pumped in or out.

3. Results and discussions

The obtained NPs are diverse in shape, as shown in Figure 1(a). The average size of these NPs is 8 nm, as revealed by the size distribution histogram shown in the inset of Figure 1(a). The high-resolution TEM image of NPs is shown in the inset of Figure 1(a), in which two parallel red lines are drawn along the adjacent crystal plane, the lattice space of 0.23 nm corresponds to the (1 1 1) distance of face-centered cubic (fcc) Pd. The selective area electron diffraction pattern of the NPs is presented in Figure 1(b), where the diffraction patterns corresponding to (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (3 3 1) are clearly seen, indicating the fcc structure of Pd NPs.

The optical extinction spectrum of the Pd NPs is shown in Figure 1(c). There is no surface plasma resonance (SPR) peak in the spectrum, similarly to the previously reported results [13]. The SPR is the collective oscillation of the conduction electrons when the NPs are irradiated by the electromagnetic wave, which causes a peak in the optical extinction spectrum. It is only until recent years that the SPR of Pd NPs was observed. The SPR peak wavelength increases linearly with the increasing NPs size [14]. Particularly, the 8 nm sized Pd NPs should display the SPR peak wavelength at 225 nm [15]. The SPR of Pd NPs is sensitive to their monodispersity, little deviation in the monodispersity can lead to the disappearance of SPR. The absence of SPR in our Pd NPs may be attributed to the deviation in the shape monodispersity.

The optical nonlinearity of the NPs in air and in hydrogen environment (i.e. the mixture of air and hydrogen at a standard atmospheric pressure) with the hydrogen volume concentration of 6.4%, 12.7%, and 18.2% are investigated through the Z-scan technique. In this technique a laser beam is focused by a lens, and the sample is moved along the beam (z axis). The sample is irradiated by an increasing intensity as it is moved to the focus. The transmitted beam is affected by the nonlinearity of the sample. At each position z, the energy of the transmitted beam is detected by a probe, which obtains the open aperture (OA) Z-scan curve. If an aperture is placed in front of the probe to block the periphery of the beam, the closed aperture (CA) Z-scan transmittance curve is obtained. The NLA can be revealed by the OA Z-scan curve, and the nonlinear refraction (NLR) can be revealed by the divided Z-scan curve which is obtained by divide the CA Z-scan curve by the OA Z-scan curve [16].

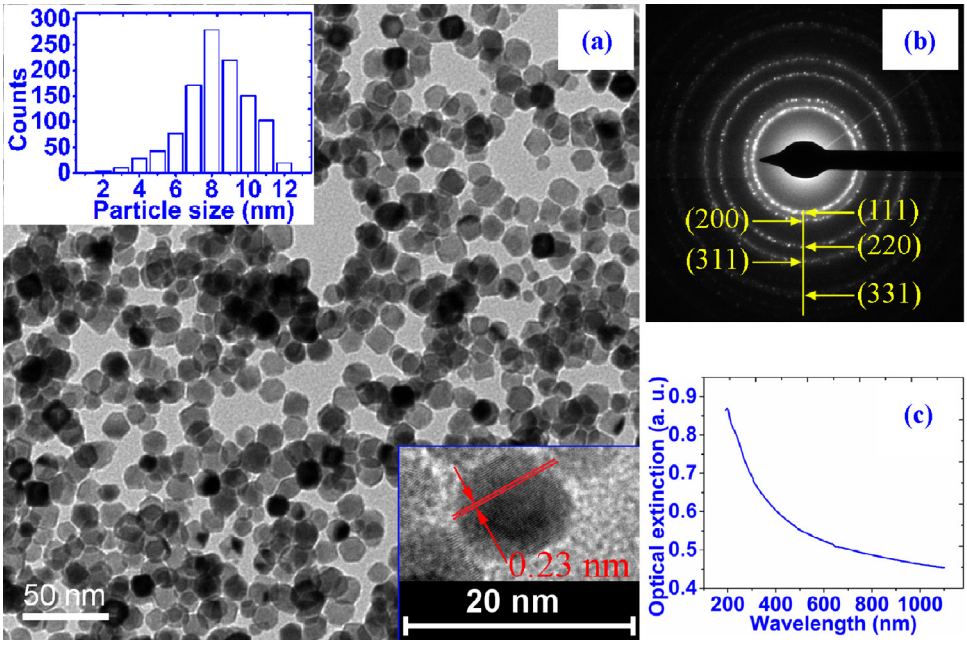

Figure 1. (a) TEM image of the Pd NPs, the size distribution histogram and HRTEM image of the Pd NPs are shown as the insets. Two parallel red lines are drawn along the adjacent crystal plane, the lattice space of 0.23 nm corresponds to the (1 1 1) distance of face-centered cubic Pd. (b) Selective area electron diffraction pattern of the Pd NPs. (c) Optical extinction spectrum of the Pd NPs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)