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Nonlinear optical absorption and refraction in Ru, Pd, and Au nanoparticle suspensions

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Abstract We present the results of studies of the nonlinear optical properties of Pd, Ru, and Au nanoparticles. We studied the nonlinear refraction and nonlinear absorption of suspensions of these nanoparticles at 1064-nm wavelength. A relatively strong nonlinear absorption of the Pd nanoparticles was observed in the case of 1064-nm, 50-ps pulses ($\beta = 2 \times 10^{-9}$ m W^{-1}). The Ru and Pd nanoparticles showed weak negative nonlinear refraction ($\gamma \sim -(6\text{–}8) \times 10^{-16}$ m^2 W^{-1}) in this spectral range. In the case of the Au nanoparticles, a saturated absorption at 532 nm dominated over other nonlinear optical processes.

The nonlinear optical properties of nanoparticles have received much attention during a long time due to applications of these media in various areas. Most frequently analyzed samples were silver and gold nanoparticles due to their variable surface plasmon resonances (SPRs) being situated in the visible range and which can be successfully explored for enhancement of the third-order nonlinear susceptibilities of these media [1–3]. In the meantime, a class of other metal nanoparticles (Pt, In, Pd, Ru, Cu, etc.) has recently shown its applicability in various areas of optics. These metal nanoparticles became of great interest due to their use in photonics, electronics, sensing, catalysis, etc. In particular, the control of the size of the nanoparticles is useful in the development of high-speed optical logic devices, gas sensors, intensifiers of luminescence, Q-switchers, mode lockers, etc. (see for example [4–8]). Most of their applications are driven from the conduction electrons of metal nanostructures, the quantum size effect, and interband and intraband transitions.

Some of these nanoparticles were studied in the past using different pulse durations and wavelengths of the probe radiation, mostly in the visible and ultraviolet (UV) ranges of the spectrum. The plasmonic properties of nanodisk arrays of Pt and Pd were studied over large size and spectral ranges in [9]. In the meantime, no evidence for bulk or surface plasmons in the range of a few eV is available in the literature for small-sized (<10 nm) Ru and Pd particles. In particular, previously it was shown that 50-nm Pd nanocubes exhibit a resonant peak at around 400 nm, while particles around 10 nm in size have no resonance between 300 and 1500 nm [10]. Recently developed methods of preparation of the triangular and hexagonal Pd nanoplates allowed demonstrating the shift of the SPR peaks from 225 nm to 530 nm [11, 12]. In the meantime, pronounced SPR peaks at ∼530 nm are commonly observed in the case of Au spherical nanoparticles.

Note the absence of reports about the plasmonic properties of Ru nanoparticles and the influence of extinction properties of these media (Pd and Ru clusters) on the nonlinear optical response in various spectral ranges. Even the variations of the SPR properties of Pd nanostructures are still unexplored. The SPR peak of small Pd nanoparticles (typically ∼10 nm in size) is assumed to be located in the UV region, which gives them a black color. As calculated using the discrete dipole approximation method or Mie theory, the resonance peak of palladium clusters of 8 nm in size should be located at about 225 nm. Note that the surfaces of Pd nanoclusters are usually covered by such protectors as polyvinyl pyrrolidone (PVP), which has an absorption peak at 212 nm. Therefore, the growth of absorption in this region is a convolution of both these species. The same can be said about the Ru nanoparticles, whose black color is also at-

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tributed to a strong plasmonic peak in the UV, taking into account that the frequency of the SPR can be spectrally tuned by changing size, shape, and dielectric environment of the particles. These broad absorption bands are due to the electromagnetic field-induced collective oscillation of the free conduction electrons occupying states near the Fermi level in the conduction band.

In this paper, we present the results of systematic studies of the nonlinear optical properties of commercially available small-sized Pd, Ru, and Au nanoparticles, as well as their structural and optical characteristics. We analyze the nonlinear refraction and nonlinear absorption of Pd and Ru nanoparticle suspensions using 1064-nm radiation of different pulse durations. We also report a saturated absorption in Au nanoparticles using 532-nm laser pulses.

The Pd, Ru, and Au nanoparticle suspensions were purchased from the Wako Pure Chemical Industries, Ltd. (Japan) and used in experiments without further purification. The initial molar concentrations of metal nanoparticles in the suspensions were 10 mM (for the gold suspension) and 20 mM (for the ruthenium and palladium suspensions). The solvents of these suspensions were water and ethanol (in the case of Pd), water (in the case of Ru), and water and n-propanol (in the case of Au). The nanoparticles were protected against aggregation by adding PVP (for Pd and Ru) and polyethyleneimine (for Au). The morphology of the nanoparticles was analyzed by transmission electron microscopy (TEM). We also measured the absorption spectra of the nanoparticle suspensions to define the appearance of the SPR.

In the case of the studies of third-order nonlinearities, these nanoparticle suspensions were analyzed using the conventional Z-scan technique [13] to measure their nonlinear optical characteristics (nonlinear refractive index γ and nonlinear absorption coefficient β). 2-mm-thick silica glass cells filled with the diluted suspensions were used for these studies. We used the radiation of a mode-locked Nd:YAG laser (1064 nm, 50 ps) to define the nonlinear optical characteristics of the suspensions. This radiation was focused by a 300 mm focal length lens. The samples were moved along the Z-axis through the focal area to observe the variations of the phase and amplitude of propagated radiation in the far field. The energy of the laser pulses was measured by a calibrated photodiode. A 1-mm aperture was placed at the distance of 800 mm from the focal plane (closed aperture scheme). The radiation propagating through this aperture was registered by a second photodiode. The closed aperture scheme allowed the determination of both the sign and the value of γ of the samples, as well as the value of β. The latter parameter was also determined using the open aperture scheme. The nonlinear optical measurements were calibrated using CS_2.

Some preliminary results of studies of the nonlinearities of Pd, Ru, and Au nanoparticle suspensions in the 800-nm range were reported in [14]. Here we present a systematic study of these parameters using 1064-nm radiation, as well as the morphological analysis of the nanoparticles.

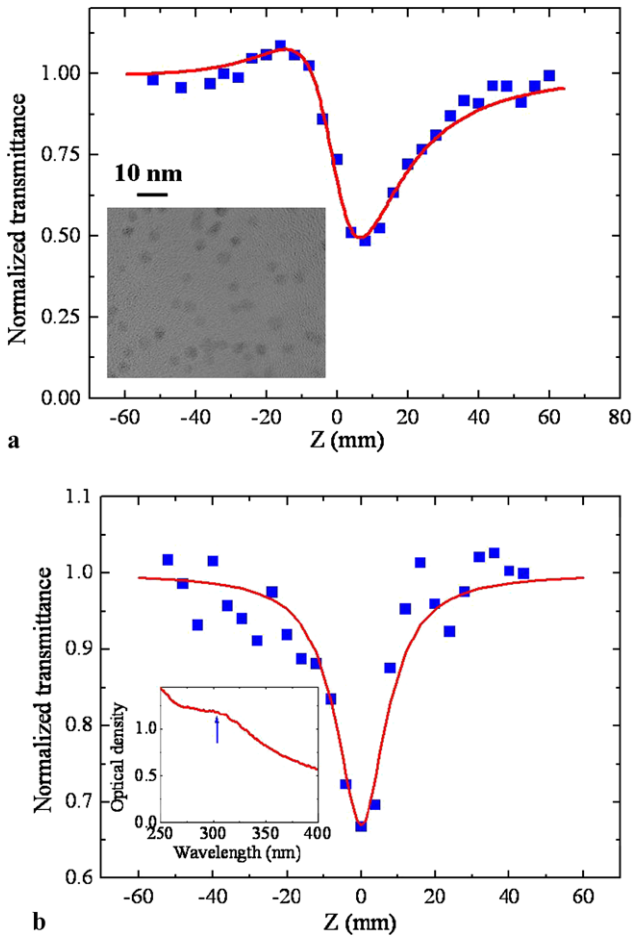


Fig. 1 Z-scans of Pd nanoparticle suspension obtained using 50-ps, 1064-nm radiation. (**a**) Closed aperture Z-scan of the Pd nanoparticle suspension. (**b**) Open aperture Z-scan of the Pd nanoparticle suspension. *Solid curves* are fitted with experimental data. The measurements are taken at the laser intensity at the focal plane of $I_0 = 1.7 \times 10^{10}$ W cm^{-2}. *Insets* show the TEM image of Pd nanoparticles and the absorption spectrum of the Pd nanoparticle suspension. *Arrow* shows the central range of the SPR absorption band of the Pd nanoparticles (305 nm). The mean size of the nanoparticles is 2.5 nm

The nanoparticle size and shape are of crucial importance when one considers the nonlinear optical processes in nanoparticle-containing suspensions, since the influence of quantum confinement on the nonlinear optical properties of the medium strongly depends on the spatial characteristics of the nanoparticles. The inset in Fig. 1a shows a TEM image of Pd nanoparticles. The mean size of the Pd nanoparticles was measured to be 2.5 nm, close to the data presented by the manufacturer (3–5 nm), with a relatively narrow particle size distribution. These structural measurements suggest that the Pd nanoparticles could exhibit the quantum confinement-induced enhancement of the nonlinear optical properties due to their relatively small sizes. The inset in

Fig. 1b presents the absorption spectrum of a Pd suspension measured using a USB2000 fiber spectrometer. Some indication of the absorption band related with the plasmon resonance is clearly seen around 305 nm.

Figure 1a shows the closed aperture Z-scan of a Pd nanoparticle-containing suspension measured using 1064-nm, 50-ps pulses. It demonstrates a weak negative nonlinear refraction, with strong indication of nonlinear absorption. In the general case, when one has the contributions of both nonlinear refraction and nonlinear absorption, the normalized transmittance dependence in the closed aperture Z-scan scheme can be presented by the equations described in [13, 15].

By defining the relative coordinate $x = z/z_0$, z_0 being the diffraction length, the spatial dependence of the normalized transmission T in closed aperture Z-scan in the case of the presence of nonlinear refraction and nonlinear absorption can be written as [15]

$$T(x) = 1 - \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi_0 - \frac{2(x^2+3)}{(x^2+9)(x^2+1)}\Delta\Psi_0. \quad (1)$$

Here $z_0 = 0.5kw_0^2$, $\Delta\Phi_0 = k\gamma I_0 L_{\text{eff}}$, $\Delta\psi_0 = \beta I_0 L_{\text{eff}}/2$, $k = 2\pi/\lambda$ is the wave number, w_0 is the beam waist radius at beam focus, I_0 is the on-axis intensity of the laser beam at the focal plane, $L_{\text{eff}} = [1 - \exp(-\alpha_0 L)]/\alpha_0$ is the effective sample length, L is the thickness of the cell filled with the nanoparticle suspension, and α_0 is the linear absorption coefficient, which was calculated from the absorption spectra of the samples. In our conditions L_{eff} was close to the thickness of the cells filled with nanoparticle suspensions, since, at 1064 nm, no considerable absorption was registered. The length of nonlinear medium considerably affects the nonlinear optical response of the medium. In our case it was 2 mm, which was less than the confocal parameter of the focused radiation (5 mm).

The best theoretical fit (Fig. 1a, solid curve), which was defined using (1), allowed calculating the nonlinear optical parameters to be $\gamma = -1.2 \times 10^{-19}$ m^2 W^{-1} and $\beta = 4 \times 10^{-13}$ m W^{-1} for the Pd nanoparticle suspension. We attribute the refractive nonlinearities observed in this study to the optical Kerr effect, while the nonlinear absorption could be related with the reverse saturated absorption and two-photon processes.

To confirm the measurements of nonlinear absorption in the Pd nanoparticle suspension, we carried out the open aperture Z-scan (Fig. 1b). The normalized transmittance in the case of the open aperture scheme can be determined as [13]

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1, \quad (2)$$

where

$$q_0 = \beta \frac{I_0[1 - \exp(-\alpha L)]}{[1 + (z/z_0)^2]\alpha}. \quad (3)$$

After fitting (2) with experimental data (Fig. 1b, solid curve) the nonlinear absorption coefficient of the Pd nanoparticle suspension was calculated to be 5.4×10^{-13} m W^{-1}, which was close to the data obtained using the closed aperture Z-scan.

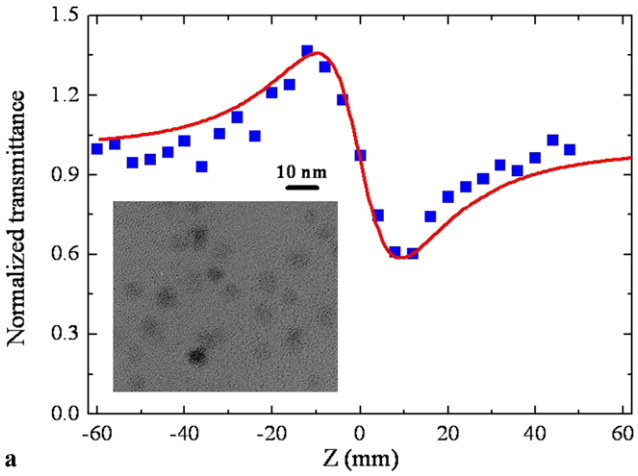
Taking into account the estimated weight part of Pd nanoparticles in the diluted suspensions (2×10^{-4}), one can calculate the nonlinear refractive effect attributed to the palladium nanoparticles ($\gamma_{\text{Pd}}^{1064} = -6 \times 10^{-16}$ m^2 W^{-1}). The corresponding nonlinear absorption coefficient of Pd nanoparticles was calculated to be $\beta_{\text{Pd}}^{1064} = 2 \times 10^{-9}$ m W^{-1}. We verified that the nonlinear optical response of water and ethanol ($\gamma < 0.5 \times 10^{-19}$ m^2 W^{-1}) was insignificant compared with the nonlinearities caused by the nanoparticles.

The left-hand inset in Fig. 2b shows the absorption spectrum of a Ru nanoparticle suspension. The absorption peak around 240 nm was attributed to the SPR of the Ru nanoparticles. Previously, the plasma absorption bands of the Ru nanoparticles, synthesized under pulsed laser ablation of bulk Ru in water, at around 254, 300, and 420 nm were observed [16]. The nanoparticle sizes (3.4 nm; see the inset in Fig. 2a) were larger compared with Pd nanoparticles. The presence of Ru nanoparticles was confirmed using energy dispersive X-ray spectroscopy (see the right-hand inset in Fig. 2b).

Application of the 1064-nm pulses caused insignificant nonlinear absorption (see the open aperture Z-scan, Fig. 2b). In the meantime, the negative nonlinear refraction caused the characteristic peak–valley pattern in the case of closed aperture Z-scan at relatively weak laser intensity (Fig. 2a). The value of γ of the suspension was calculated to be -3×10^{-19} m^2 W^{-1}. In the case of the Ru nanoparticle suspension, the estimated volume part of metal nanoparticles was 4×10^{-4}. The corresponding nonlinear refractive index of Ru nanoparticles measured using closed aperture Z-scan was calculated to be $\gamma_{\text{Ru}}^{1064} = -8 \times 10^{-16}$ m^2 W^{-1}. The role of PVP in liquids was analyzed in [17] and no obvious nonlinear absorption and refraction effects were found. This indicates that the nonlinear processes arise mainly from Ru nanoparticles.

The Au nanoparticles (15–30 nm, see the left-hand inset in Fig. 3) showed mostly spherical shape, while in some cases we observed the triangular form of these clusters. The right-hand inset in Fig. 3 shows the absorption spectrum of an Au nanoparticle suspension. The absorption peak around 530 nm corresponds to a commonly reported SPR of the Au spherical clusters.

We did not observe nonlinear optical processes in the Au nanoparticle suspension in the case of 1064-nm probe



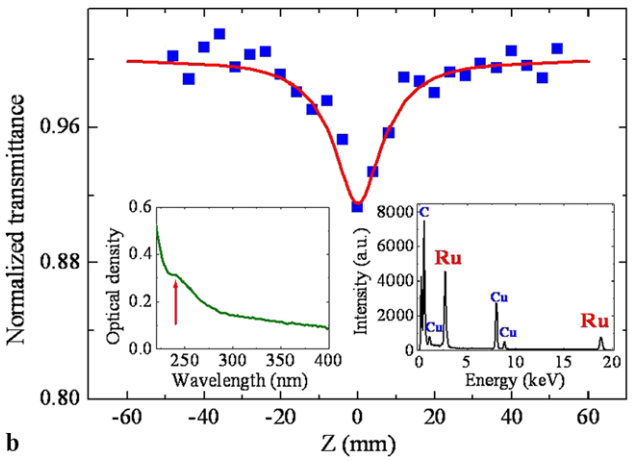


Fig. 2 Z-scans obtained using 50-ps, 1064-nm radiation. (**a**) Closed aperture Z-scan of Ru nanoparticle suspension. (**b**) Open aperture Z-scan of Ru nanoparticle suspension. *Solid curves* are fitted with experimental data. The measurements are taken at the laser intensity at the focal plane of (**a**) $I_0 = 9 \times 10^9$ W cm^{-2} and (**b**) $I = 1.7 \times 10^{10}$ W cm^{-2}. *Insets* show the TEM image of Ru nanoparticles, the absorption spectrum of the Ru nanoparticle suspension, and the energy dispersive X-ray spectrum of the Ru nanoparticles supported by a carbon film on a copper grid. *Arrow* shows the central range of the SPR absorption band of the Ru nanoparticles (240 nm). The mean size of the nanoparticles is 3.4 nm. Additional lines in the energy dispersive X-ray spectrum originate from the support material

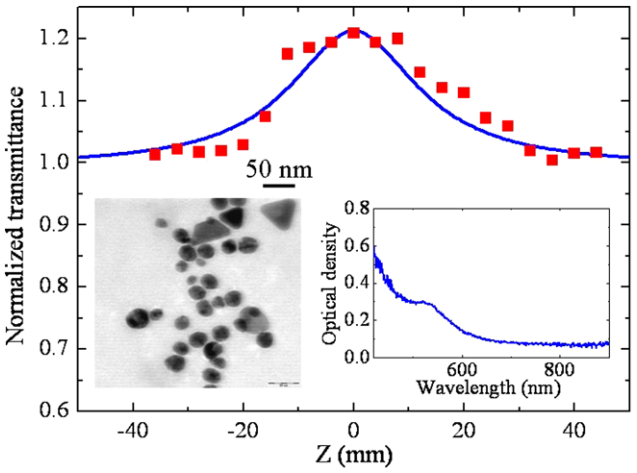


Fig. 3 Open aperture Z-scan of Au nanoparticle suspension obtained using 50-ps, 532-nm radiation. *Solid curve* is fitted with experimental data. *Insets* show the TEM image of Au nanoparticles and the absorption spectrum of the Au nanoparticle suspension. The mean size of the nanoparticles is 20 nm

radiation. At the same time, we observed a saturated absorption in this medium in the case of 532-nm laser pulses. Note that previously a weak negative refraction and a positive nonlinear absorption in Au nanoparticles using 792-nm radiation were reported [14]. Figure 3 presents the open aperture Z-scan of the Au nanoparticle suspension at a molar concentration of 0.2 mM. In these experiments ($I \approx 3 \times 10^{10}$ W cm^{-2}), the characteristic dependence of negative nonlinear absorption was observed. The Au nanoparticle suspension did not show a refractive nonlinearity, while it demonstrated a saturated absorption. Performing closed aperture Z-scan with 532 nm for the Au sample did not yield any result—probably because as the SPR of Au lies at around 530 nm, the high saturated absorption at 532 nm totally masks the other effects. A standard fitting procedure allowed defining a saturated intensity and a negative nonlinear absorption coefficient of this suspension (9×10^9 W cm^{-2} and -8×10^{-13} m W^{-1} respectively). The appearance of saturated absorption could be caused by bleaching of the ground state at moderate intensities.

The experiments were carried out using the picosecond pulses at 2-Hz pulse repetition rate. In these conditions, no influence of thermal effect can be distinguished, taking into account very small linear absorption at 1064 nm for Pd and Ru samples. As for the Au sample probed by 532-nm pulses, we carried out analogous measurements using single pulses. No difference was observed in that case compared with the 2-Hz pulse repetition rate.

The Kerr-induced effect, which is due to the electronic response of the particles, seems to be the most important optical process contributing at short laser pulses to the nonlinear refraction of nanoparticles. The nonlinear contribution to the refractive index in appropriate experimental conditions can also be due to the thermal effect. This effect consists of two parts: one is the 'fast' process of acoustic wave propagation, and the other is the 'slow' steady-state changing of the medium density due to accumulative thermal heating of the absorbing area. The slow process should be taken into consideration at low thermal conductivity and/or high pulse repetition rates. The fast process causes the matter density variations due to acoustic wave propagation after local heating. The rise time (τ), which is necessary for observing the density variations and further the refractive-index variations, is determined by the ratio of the beam waist radius at the focal point to the sound velocity in the medium (V_s);

$\tau = w_0/V_s$. Taking into account our experimental conditions ($w_0 = 28$ μm for 50-ps pulses at the wavelength of 1064 nm, V_s in water approximately 1500 m/s), a rise time can be estimated as $\tau \sim 20$ ns, which is almost three orders of magnitude longer than the laser pulse, i.e. the influence of the thermal effect should be neglected in the case of our experiments.

Past studies of the optical nonlinearities of some nanoparticles, particularly Pt nanoparticle suspensions, showed the presence of reverse saturated absorption [17], while the changeover from saturated absorption to reverse saturated absorption in Pt nanoparticles was reported in [14, 18] using 532-nm and 795-nm radiation. The change from saturated absorption to reverse saturated absorption in gold nanoclusters was also reported in [19]. These two processes were attributed to the bleach of the ground state occurring at moderate intensities and transient absorption caused by free carriers, which is significant at higher pump intensity. The saturated absorption of Ag nanoparticles embedded in silica glass matrices has previously been observed as far as 355 nm. This process has also been reported in Ag:water suspension in the case of 397.5-nm, 1.2-ps radiation [20, 21]. The saturated absorption of a platinum nanoparticle suspension was analyzed using 1064-nm, 50-ps pulses at different intensities of laser radiation [8]. The concurrence of reverse saturated absorption and saturated absorption at high intensities allowed for defining the saturated intensity for different suspensions of Pt nanoparticles. This suspension was used for the mode locking of laser radiation in a Nd:glass laser ($\lambda = 1054$ nm).

Previous measurements of nanoparticles' nonlinearities depended on the methods of preparation, aggregation, concentration, sedimentation, and other physical processes influencing the nonlinear optical response of the medium under investigation. In this paper, we for the first time show the nonlinear optical measurement of rarely investigated nanoparticles possessing stable morphology, which allows repeateable measurements. The studies in the infrared (IR) range, which give a noticeable nonlinear response from nanoparticle-containing suspensions, allowed us to assume that, even quite far from the plasmon resonances, the nanoparticles possess a strong nonlinear response. Our studies show that not only local field enhancement in the vicinity of the SPR can influence the nonlinear optical response of such samples, but other processes could also be involved in the enhancement of their nonlinear optical parameters.

In conclusion, we presented the results of studies of the nonlinear optical characteristics of commercially available Pd, Ru, and Au nanoparticles, as well as their morphological and optical parameters. We analyzed the nonlinear refraction and nonlinear absorption of suspensions of Pd and Ru nanoparticles using 1064-nm radiation. There was found a relatively strong nonlinear absorption of Pd nanoparticles in the case of 1064-nm pulses ($\beta = 2 \times 10^{-9}$ m W^{-1}). The Ru and Pd nanoparticles showed a negative nonlinear refraction ($\gamma \sim -(6\text{–}8) \times 10^{-16}$ m^2 W^{-1}). The negative nonlinear absorption (i.e. saturated absorption) was observed in the case of the Au nanoparticle suspension.

These studies have shown that the quantum size effect should not play much role in the enhancement of the third-order nonlinear optical characteristics of Pd and Ru nanoparticles in the near-IR range (1064 nm), due to the SPRs of these samples (240 nm and 305 nm) being positioned quite far from the wavelength of the Nd:YAG laser. The comparison of these media with the gold nanoparticles, whose plasmon resonance (∼530 nm) coincided with the excitation wavelength (532 nm), showed considerably higher nonlinear optical response in the latter case. Thus, for achieving stronger nonlinear optical response in Pd and Ru nanoparticles one has to use shorter wavelength sources (for example, the fourth harmonic of a Nd:YAG laser, $\lambda = 266$ nm). In the meantime, there is a strong linear absorption at 266 nm, in both water and surfactant. The SPRs of Pd and Ru will be masked by linear absorption and SPR of the surfactant. Our aim was to show a strong nonlinear optical response at $\lambda = 1064$ nm (i.e. far from the SPRs) for the nanoparticles under consideration, which are the new objects of investigation. Note that even at low energy of the probing photons (1.17 eV), Pd and Ru nanoparticles showed nonlinear refraction and relatively strong nonlinear absorption.

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