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Optical features of the gold nanoparticles deposited on ITO substrates

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ABSTRACT

We have performed firstly studies of the photoinduced second order susceptibilities in the Au nanoparticles (NP) A, B and C under simultaneous influence of the bicolor 1064 nm and bicolor laser treatment (1064 nm 10 ns pulsed laser with pulse power densities 532 nm 10 ns laser treatment and the cw 300 mW 532 nm SHG coherent laser beams. We have studied three types of samples possessing irregular and different dense parameters of the Au NP deposited on the ITO substrate. We have found that the maximal bicolor (1064 nm and 532 nm) stimulated optical second harmonic generation for the 10 ns pulse duration was observed for the samples possessing irregular Au NP deposited on the ITO. We have performed studies of the photoinduced second order susceptibilities in the Au NP under simultaneous influence of the bicolor 1064 nm and bicolor laser treatment (1064 nm 10 ns pulsed laser with pulse power densities 532 nm 10 ns laser treatment and the cw 300 mW 532 nm SHG coherent laser beams). We have found that during the 15–20 min of the cw treatment there occur the principal changes in the absorption maxima. These maxima indicate on the occurrence of the additional absorption nearby the 308 nm and 310 nm and 345 nm spectral bands. The later are caused by the occurrence of the trapping levels in the border between the ITO substrate and the Au nanoparticles.

1. Introduction

Recently one can observe an enhanced interest to the studies of the nonlinear optical effects in the gold nanoparticles [1–4]. Besides the relatively high third order susceptibilities in the such type of the films they possess exceptional photoinduced changes which are caused by plasmon-induced charge separation under visible light irradiation on deposited Au nanoparticles (Au NP) has been reported for TiO_2 film electrodes [5,6] and was explained by the electron transfer from the photoexcited gold nanoparticles to the dielectric substrates, like TiO_2. It is particularly important to enhance the second order susceptibilities in particularly second harmonic generation which occur on the interfaces between the nanoparticles and the dielectric substrates [7]. In the Ref. [8] following the dependence of the quadratic hyperpolarizability on the particle size, it was established that retardation effects of the electromagnetic fields play a major role in the frequency conversion process. The harmonic response is dominated by the dipolar contribution arising from the deviation of the particle shape from that of a perfect sphere. It is therefore concluded that the origin of the nonlinear polarization for the smaller silver particle sizes arises from the surface similar to the case of the gold metallic particles. For larger diameter particles, retardation effects in the interaction of the electromagnetic fields with the particles cannot be neglected any longer, and the response deviates from the pure dipolar response, exhibiting a strong quadrupolar contribution.

In Ref. [9] it was found that second harmonic light can be generated from a diffraction grating of gold nanoparticles with planar inversion symmetry. By measuring the angular distribution of the second harmonic light, we observe an effect in which the diffraction pattern of the grating is superimposed on the intrinsic second harmonic radiation pattern of the nanoparticles. This result suggests that the second harmonic generation may be used to study coherent nonlinear optical effects in symmetric as well as asymmetric metal nanoparticles. Following a nonlinear scanning near-field optical microscope (SNOM) [10] it was discovered that the near-field nonlinear response is directly related to the local surface plasmon resonances and to the particle morphology. Nanoscale changes in the local fields and material properties give opportunity to use higher-multipole (magnetic-dipole and electric-quadrupole) contributions to the nonlinear response in addition to the electric-dipole contributions. Moreover, the local-field distribution is crucial to obtain sufficient interaction with the locally-varying nonlinearity. Local-field enhancement is particularly important for nonlinear optical effects. Extremely small features of a few nm, such as nanogaps

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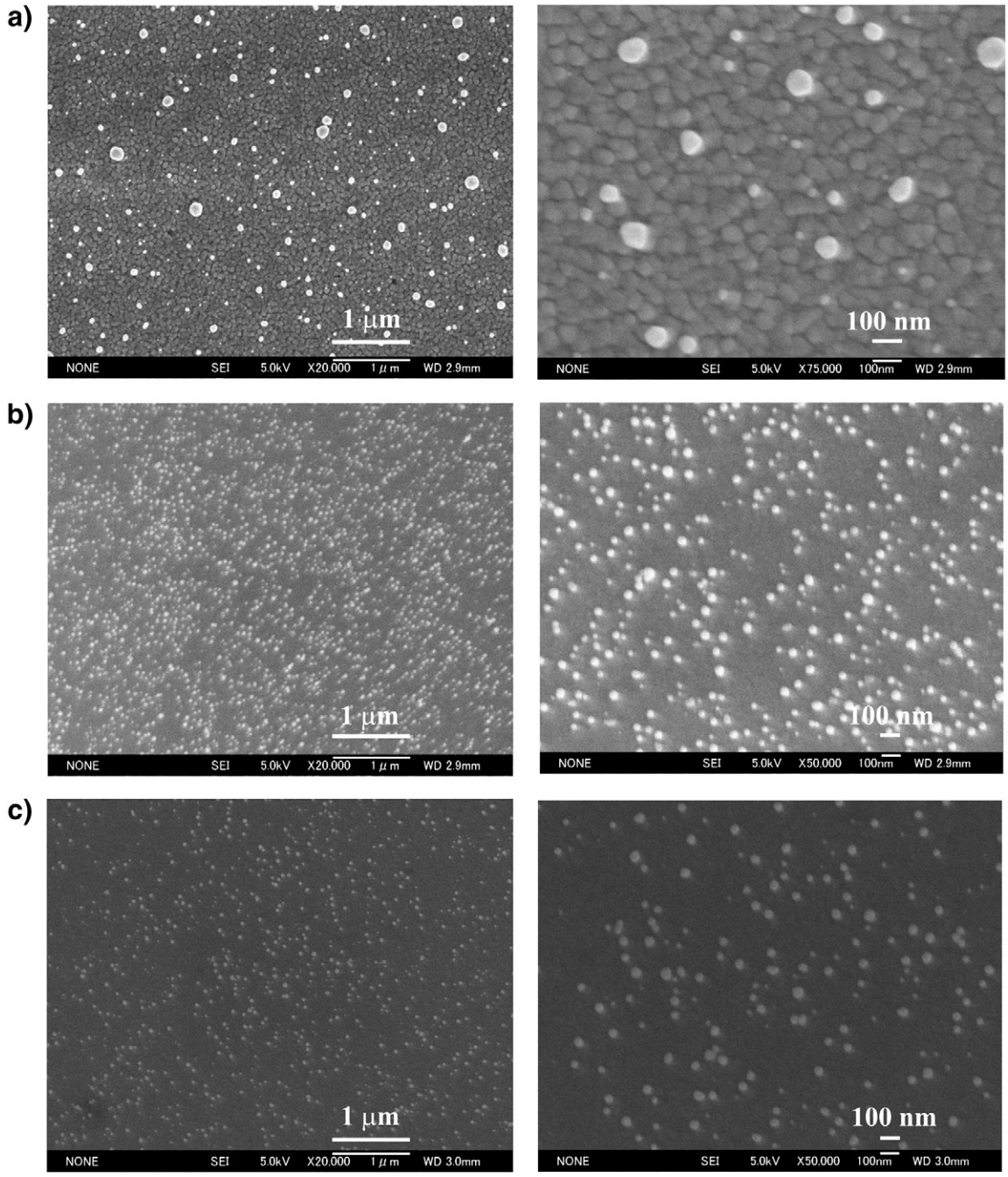

Fig. 1. SEM surfaces of the samples prepared following the procedures: a) 1; b) 2; and c) 3.

between two particles, are particularly beneficial for field localization and enhancement. Following these reasons it is a principal difference between the second harmonic generations in the gold nanoparticles with respect to the usual second harmonic generation which needs sufficiently large optical power densities [11].

To form additional non-centrosymmetry which will suppose on the surface plasmon resonances in Ref. [12] it was proposed to use ITO substrates possessing different resistivity sweet to operate by the interface charge transport between the nanoparticles and the dielectric substrate. It was shown a marked dependence on the inter-particle distance and density. It was shown that the decrease of the inter-particle distance with the increase of Au nanoparticle density favors the photoinduced optical second harmonic generation. The predominant role of the interface between the Au nanoparticles and the ITO substrate is shown. Following the reasons presented above one can expect that additional cw-laser treatment at the wavelengths near the surface plasmon resonances.

In Section 2 are the given experimental details.

2. Results and discussion

For the preparations of Au NP-attached ITO electrodes, we used two different methods. One is the seed-mediated growth method (procedure 1), the details of which have been already reported [13]. By controlling the growth time, relatively sparse attachment and growth of lower density was performed.

The other is an in-situ direct reductive attachment method. In this method, after immersing an ITO substrate into the solution of $HAuCl_4$, the solution of ascorbic acid was added to start the in-situ reductive formation of Au NPs on the ITO surface. Interestingly, the density of

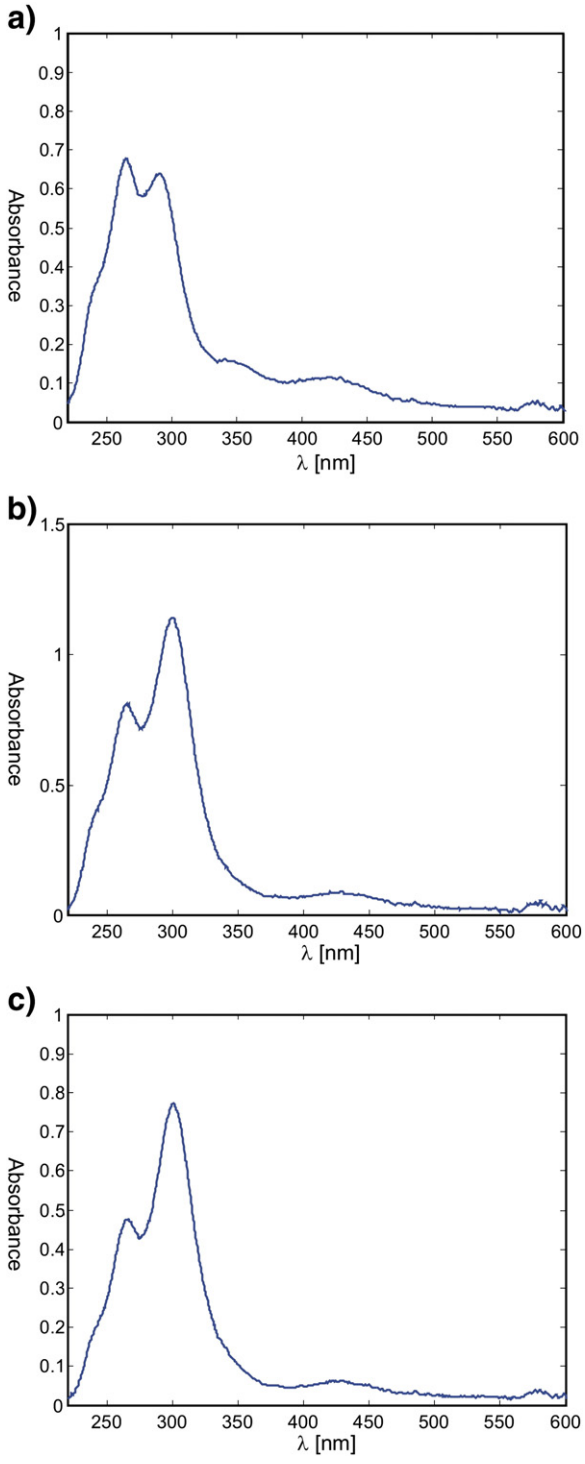

Fig. 2. Absorption spectra of the samples: a) A; b) B; and c) C.

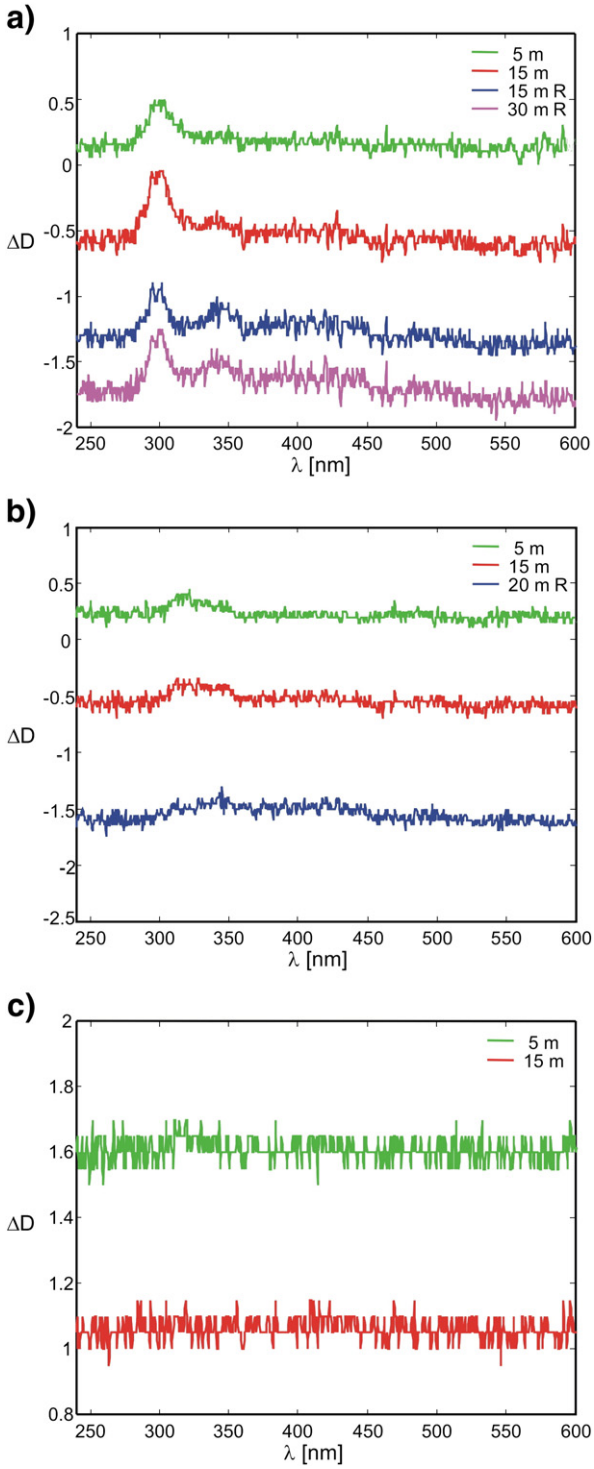

Fig. 3. Photoinduced changes of the absorption for the samples: a) A; b) B; and c) C.

attached Au NPs could be changed by the heat treatment after the addition of ascorbic acid. For preparing a densely attached surface, the temperature of the mixed solution was heated at ca. 75 °C (procedure 2). On the other hand, the sample treated at room temperature (procedure 3) showed relatively less attachment of Au NPs as shown later. The detail of this preparation method will be published elsewhere.

Fig. 1a–c show typical SEM images of the surfaces of the samples prepared following the procedures 1, 2 and 3 which we indicate by A, B and C. Reflecting the different preparation method, some essential changes can be found concerning the size regularity and density of Au NPs between Fig. 1a, b, and c. For the latter cases, some control of the density of Au NPs was possible by changing the treated temperature as described in the experimental section.

From Fig. 2a one can see that there occur several absorption maxima situated at 350 nm and 425 nm and less strong maximum at 575 nm. Photoinduced changes of the absorption for the sample A is presented in Fig. 3a. One can clearly see an occurrence of the sharp absorption at 308 nm and 310 nm and 345 nm maxima. Moreover during the first maximum is appeared just after the first 5 min. of the cw treatment. The second one at 340 nm is observed at about 345 nm.

From Fig. 4 one can clearly see that for the sample A there is a drastic increase of the second order susceptibility up to 1 pm/V during

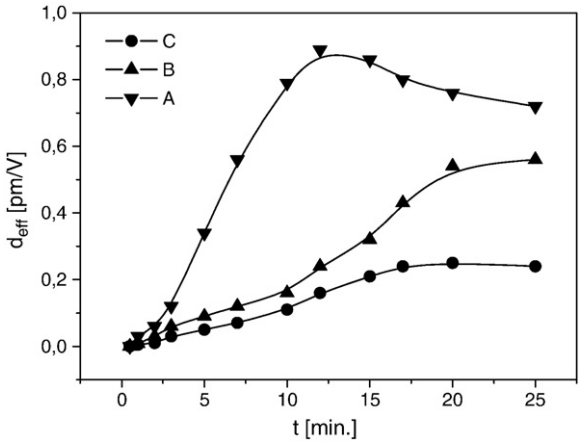

Fig. 4. Photoinduced changes of the second order susceptibility for the samples A, B and C.

the first 12 min of the optical treatment. At the same time for the samples B and C this increase is substantially less and a maximum is absent. One can say about a correlation between the occurrences of the additional photo-absorption oscillators (see Fig. 3a–c) and the values of the second order susceptibilities induced by cw all-optical poling.

Following the general presentation one can expect that here the principal role will play surface plasmon resonances for the gold and the density of the Au NP. However, in this work we demonstrate that the sensitivity of the trapping levels determining the absorption bands indicated as A, B and C is substantially stronger than the SPR maxima situated at 560 nm. Because the effect is absent for the Au NP itself as well as in other substrates one can expect that the principal role here play the nano-interfaces which effectively form the large number of nano-trapping levels situated within the forbidden energy gap, how it was shown in semiconductors layers on the ITO substrates [14]. Following the general presentation the metallic nanoparticles may be of interest also for the different rare earth doped glasses. Additional factor responsible for the observed phenomena may be caused by photoinduced exciton states [15].

It should be emphasized that the principal role in the observed effects play nano-interfaces giving additional flattering of energy bands [16]. This factor favors also enhanced dipole moments determining the corresponding hyperpolarizabilities. As a consequence substantial role begin to play multi-photon excitations which favors occupation of the existed states responsible for the observed nonlinear optical effects [17].

3. Conclusions

We have found that during the 15–20 min of the cw treatment there occur the principal changes in the absorption maxima. These maxima indicate on the occurrence of the additional absorption nearby the 308 nm and 310 nm and 345 nm spectral bands. The relative changes of the absorption maxima correlate well with the maximally achieved optically stimulated second harmonic generation. It was found that the maximal signal of the optical second harmonic generation was observed after the 12 min of the 0.7 MW bicolor laser treatment. The samples with the regular structure show substantially less maximal values of the effective optical second order susceptibility and before the photo-damage there were any absent changes.

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