# Gold nanoparticles deposited on fluorine-doped tin oxide substrates as materials for laser operated optoelectronic devices

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Abstract We have discovered occurrence of strong narrow spectral lines in gold nanoparticles deposited on fluorine-doped tin oxide substrates at wavelengths 410, 440 and 550 nm under influence of 808 nm wavelength laser illumination with power about 200 mW. These lines appear just after the 1 s of illumination and are almost unchanged during all the remaining time of illumination. Such lines are absent for the other content of gold nanoparticlesmodified substrates. So a principle role here is played by the inter-particle distances. The relaxation process is continued during 8–10 h and the samples return to their initial states. The occurrence of the such narrow spectral lines may be a consequence of the two-photon absorption related with the corresponding electron-phonon interactions due to specific interactions between the plasmons and the phonon subsystem and the free carriers.

## 1 Introduction

Recently one can find an enhanced interest to the studies of the photoinduced changes in the gold nanoparticles (AuNPs) [1]. The surface plasmon resonance, a unique

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phenomenon to plasmonic (noble metal) nanoparticles leads to strong electromagnetic fields on the particle surface and consequently enhances all the radiative properties such as absorption and scattering. Additionally, the strongly absorbed light is converted to heat quickly via a series of non-radiative phonon-assisted processes [2]. Particular interest present their non-linear optical features [3– 7]. The corresponding effects of the second- as well as third order are caused by interaction of the surface plasmon resonances with the external light. Additional role here is played by the phonon sub-system and the trapping levels on the border between the nanoparticles and the substrate.

For the Au NP particularly interesting is spectral range within the 480–520 nm. As a consequence the observed absorption band results from the interference of the relatively power incident photons and the collective oscillation of free electrons interacting with phonons. A better understanding of the factors controlling the absorption response of the nanoparticles is crucial for the interpretation of experimentally obtained spectra. Generally these processes [8] may be defined by transfer of electromagnetic wave between the excited collective plasmonic interactions to the relatively localised interface trapping levels which form long-lived metastable states after initial illumination.

Particular interest presents the photoinduced changes in the AuNPs because in this case we observe an interaction of the external photoinducing relatively power laser light with the surfaces of the samples and additionally we can achieve the changes of the gating period [9]. Generally we are able to vary the three principal parameters: the wavelength for the photoinduced beam, its intensity, time of illumination and as a consequence we able to operate by efficiency of interactions between the electromagnetic wave surface plasmon collective excitation and the phonons. The latter ones are determined by the surrounding environment. Particularly interesting here is the seed mediated method for the AuNP-modified ITO sample preparation. Following the general [10] presentation their properties will be determined by the efficient sequence between the excited beam and the electron, plasmon and surface excited states. We are able to operate by these parameters varying the Au NP content and searching the materials in which we should obtain relatively narrow resonance presenting the effect of interactions of the plasmons and the trapping levels, in particularly nanotrapping levels and the phonons.

#### 2 Experimental

Fluorine-doped tin oxide (FTO) coated glass slides, whose sheet resistance was ca. 15  $\Omega$ /sq., were purchased from Flexitec, Brazil. HAuCl<sub>4</sub> and trichloroethylene were purchased from Sigma-Aldrich, and other reagents from Wako Chemicals, Japan. First, a FTO substrate was cleaned with trichloroethylene, ethanol and water successively. Next, the FTO substrate was immersed into 2.5 mL solution of HAuCl<sub>4</sub> (aq.) in a test tube, and subsequently 2.5 mL aqueous solution of ascorbic acid was added into the test tube. Then, the reaction mixture was heated at 75 °C for 15 min for preparing a AuNP-attached FTO substrate. Figure 1 shows the FE-SEM images of AuNP-attached FTO prepared when the concentration of HAuCl<sub>4</sub> was 2.68 mM, which were recorded using a JSM-7400F fieldemission scanning electron microscope (JEOL, Japan). Dense attachment of AuNPs was confirmed from the FE-SEM images.

The process of illumination and measurement of the photoinduced absorption was performed using the 20 mW 808 nm laser with beam diameter varying between the 4–5 mm. The spectroscopic measurements were performed during use of the optical fiber Ocean Optics spectrometer.

This spectrometer with spectral resolution up to 0.2 nm allow to perform the spectral measurements directly after the illumination. To achieve the high stability of the laser system a special system of photo-control feedback was used. This one allows to achieve the stability of the laser power within the 0.08 %. The use of the line detector arrays allow to obtain the high resolution spectra which were changed during the phototreatment as well as after the switching off of the laser beam. Among the different materials we have chosen the Au NP deposited on the ITO surfaces for which we have achieved the discrete photoinduced changes which are presented in the Fig. 1.

## 3 Results and discussion

Following the results presented in the Fig. 2 one can clearly see that the occurred narrow spectral maxima for the photoinduced absorption at wavelengths 404, 440 and 510 nm may be caused by specific interaction of the photoinduced cw laser 808 nm beam with the Au NP/FTO nanocomposites. Moreover in the Fig. 3 is shown the power dependence of eh line at 404 nm which show a drastic jump at about 160 mW. This may indicate on an occurrence nonlinear optical features of the process. It is interesting that the first maximum corresponds exactly to the doubled frequency photoinducing beam and is equal to about 404 nm. Two another maxima may be caused by combination of the laser induced beam with the doubled frequencies beams.

These effects may be connected by interaction of the relatively strong light with the plasmons and the further interactions with the phonons [11, 12]. Moreover, the greatly enhanced local field intensities can lead to drastic enhancement of two-photon like absorption processes, potentially allowing much lower incident radiation intensities to be used. As a confirmation of the such models the



Fig. 1 FE-SEM images of AuNP-attached FTO substrate recorded with low and high magnifications. The sample was prepared when  $[HAuCl_4]$  was 2.68 mM

2

0

9



Fig. 2 Changes of the spectral optical density induced by 808 nm 200 mW laser with time. Two dimensional presentation



Fig. 3 Pump intensity dependence of the 404 nm spectral line versus the power density

excited states exist during 8–10 h and only after begin to relax. This may be a consequence of de-occupation of the SPR laser stimulated trapping levels de-occupation in times. This may be a coincidence of the two-photon absorption with the following fluorescence [13] which is trapped by the Au NP/FTO states.

The second tour of laser treatment demonstrates the existence of the completely irreversible process. So one can exclude existence of some photo-structural damages which may be responsible for the effect. Only pure electronic contribution interaction with the plasmons and phonon relaxors are here principal.

The general features of the obtained photoinduced twophoton absorption indicate that there are relatively spectrally narrow line. So contribution of the bothering factors like electron–phonon interaction and the scattering of the



Fig. 4 3D presentation of the time kinetics for the photoinduced absorption



Fig. 5 The photoinduced 3D kinetics after the 808 nm laser illumination

laser light do not play here a crucial role. The spectra asymmetry also is not so huge which allow to predict that in this case the different intra-band dopants do not play essential role. The complete reversibility of the effect is caused by the absence of the long-lived metastable level. The spectral topography of the observed changes (Figs. 4, 5) may be explained by fulfilling of corresponding collinear nonlinear interactions.

It is crucial that illumination by other wavelengths and on the samples with different matrices did not manifest this effect. The changes were more smooth, similarly to the [7] and in all the cases the multi-photon processes are similar to the observed in the [14].

The presented results confirm that the studied films may be of huge interest for the optically induced electronic devices [14-17].

## 4 Conclusions

We have established an occurrence of narrow spectral maxima in gold nanoparticles deposited on fluorine-doped tin oxide at wavelengths 404, 440 and 510 nm which may be caused by specific interaction of the photoinduced cw laser 808 nm beam. It is interesting that the first maximum

corresponds exactly to the doubled frequency photoinducing beam and is equal to about 404 nm. Two another maxima may be caused by combination of the photoinducing beam with the doubled frequencies beams. These effects may be connected by interaction of the relatively strong light with the plasmons and the further interactions with the phonons. It is crucial that illumination by other wavelengths and on the samples with different matrices did not manifest this effect.

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