Femtosecond transient absorption of plasmonic gold nanoparticles embedded in mesoporous TiO$_2$ matrix: electron injection study

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ABSTRACT

Femtosecond transient absorption spectra of gold nanoparticles embedded in mesoporous TiO$_2$ films were studied by a laser photolysis pump – probe technique using 25 fs pulses at 740 nm (1.68 eV). The shift of the bleaching peak in transient spectra of order of 100 meV is detected for AuNP/TiO$_2$, whereas the bleaching peak shift of the same AuNPs in aqueous colloids does not exceed 5 meV. The initial shifts do not depend on power (30 nJ – 300 nJ) of the pump pulse. The shift direction is in agreement with the model of positively charged AuNPs even for time delays of order of 30 fs which suppose ultrafast electron injection from AuNP to TiO$_2$ matrix on the same time scale.

Keywords: nanoplasmonics, femtosecond pump-probe spectroscopy, titanium dioxide, gold, electron injection

1 INTRODUCTION

Surface plasmon resonances (SPR) of metallic nanoparticles are the subject of great interest due to the multitude of applications enabled by locally enhanced electric fields and nonlinear optical phenomena mediated by them [1]. Gold nanoparticles (AuNP) embedded in mesoporous films of wide band gap semiconductors such as TiO$_2$ are used for promising applications in solar cells, visible light-sensitive photocatalysts, and biosensors developed on the basis of the surface plasmon resonance properties of metal nanoparticles (NP) [2]. Femtosecond laser sources have made it possible to temporally resolve electron–electron and electron–phonon dynamics under a variety of excitation conditions in colloids and dielectric glasses [3-5].

Contact between AuNP and TiO$_2$ could be a reason of the additional mechanism of electron relaxation in plasmonic nanoparticles related to the charge transfer that manifests itself as specific features of femtosecond transient absorption spectra of the system. The last question is studied in this work.

2 SAMPLE PREPARATION

AuNPs were prepared by standart routine described by Turkevich and Frens [6]. The reduction of a gold hydrochlorate solution (Aldrich, 99%) has been initiated by sodium tris-citrate (Merck) by bringing gold solution to a boil in a double-walled reactor. 2 ml of 38.8 mM of Na$_3$Cit were added to heated 20 ml of 1mM HAuCl$_4$. The mixture was boiled during 10 min.

The following procedure was made to produce Au/TiO$_2$ mesoporous films. 4.6 ml of titanium isopropoxide was added dropwise to 24 ml of an aqueous 0.1M HNO$_3$ with vigorous stirring. The resulting suspension was rapidly heated to 75°C until almost transparent colloidal solution was formed. The solution was filtered through a syringe filter (0.2 µm) in a teflon vessel in a steel autoclave and heated in a furnace at 200°C during 12 hours. Polyethylene glycol 20M was added to TiO$_2$. Weight ratio was PEG:TiO$_2$ = 0.2:0.8. TiO$_2$ paste and the solution of colloidal gold were mixed in volume ratio of 1:80. Mixture was centrifuged at 10,000 rev /min for 5 min. Colored paste was rolled to a "soda-lime" glass by doctor blade technique. After drying for 20 minutes at room temperature the films were annealed in a muffle furnace at 450°C for 0.5h. The film thickness was about 8 µm. The morphology of the produced film as well as size distribution of AuNP is shown on Figure. 1
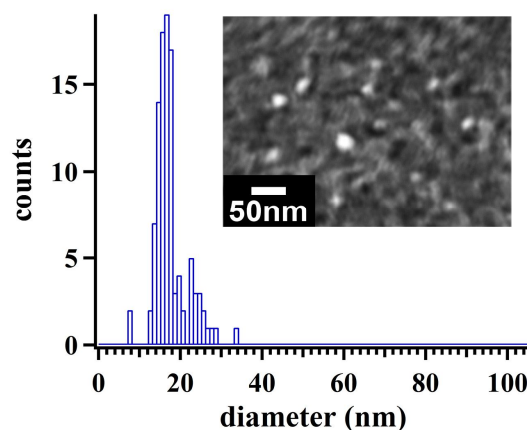

Figure 1: Size distribution of AuNPs in TiO$_2$ film (SEM scan included).

3 EXPERIMENTAL SETUP

Transient absorption spectra were measured by the femtosecond pump-supercontinuum probe setup [7]. Femtosecond pulses were generated by "Tsunami" (Spectra Physics) solid-state titanium-sapphire laser (τ = 80 fs, E = 0.8 nJ, λ = 802 nm, f = 80 MHz) pumped by «MilleniaVs» (Spectra Physics) diode-pumped continuous solid-state laser (λ = 530 nm, P = 4.65 W). After amplification in the regenerative amplifier ("Spitfire", Spectra Physics)

femtosecond pulses had following parameters: τ = 90 fs, E = 1200 µJ, λ = 805 nm, f = 1 kHz. The amplified radiation was divided into beams in order to prepare the pump and probe pulses. First beam which used as a pump was directed into delay line which has delay time up to 60 ps, with a minimal time step of 3.3 fs. After that, the laser pulse was directed to noncollinear parametric light amplifier ("NOPA" Clark MXR) which converted the carrier wavelength 805 nm to wavelength λ = 740 nm (τ = 25 fs, energy could be varied from 0 to 400 nJ). The diameter of pump spot was 300 µm.

The power of the second beam was decreased to an energy ~ 0.5-2 µJ and focused into water cell for supercontinuum generation. Supercontinuum pulse has spectral range of 400-1000 nanometers. The total energy of the pulse was less than 10 nJ. Then supercontinuum pulse was divided into two channels: the probing pulse and the reference pulse. The signal registration was carried out using polychromator "Acton SP-300" and CCD-camera "Pixis 100" (Princeton Instruments). The diameter of probe spot was 100 µm.

The relative polarizations of pump and probe beams were adjusted to 54.7° (magic angle) configurations. Absorption difference spectra $\Delta A (t, \lambda)$ were recorded over the spectral ranges of 400–740 nm. The measured spectra were corrected for group delay dispersion of the supercontinuum following the procedure described in [7].

4 RESULTS AND DISCUSSION

The average size of TiO_2 and Au nanoparticles was estimated as 15 nm and 16 nm, respectively (Figure.1). According to the substance concentration used while the production of Au/TiO_2 nanocomposites the average distance between AuNP of the film is 15 nm, i.e. each AuNP was surrounded by TiO_2 nanopaticles.
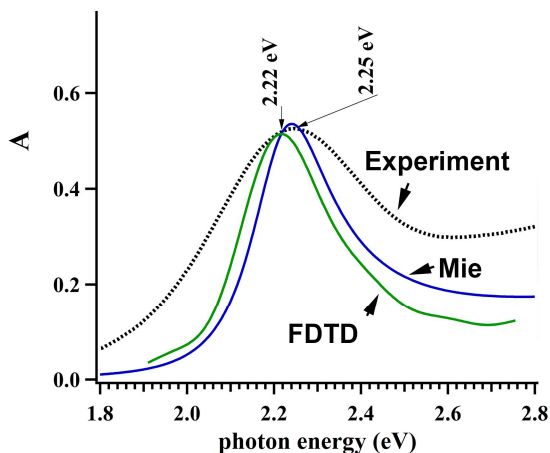
Figure 2: Experimental and theoretical absorption spectra of Au/TiO_2 nanocomposites.

In this case the coupling between Au NPs is weak [8], i.e. absorption spectrum of Au/TiO_2 can be found by Mie theory [9]. However, the surrounding medium of spherical nanoparticals must be uniform in Mie approximation. Taking into account that the size of TiO_2 nanoparticles is considerably smaller than visible wavelengths one can consider TiO_2 matrix as a uniform medium with effective permittivity. The last one can be obtained experimentally and occurred to be close to $\varepsilon_{eff} \approx (1.7)^2$, whereas the permittivity of pure TiO_2 (anatase) for visible wavelength range is $\varepsilon_{TiO_2} \approx (2.4)^2$. The substitution of ε_{eff} for Mie theory and ε_{TiO_2} for FDTD calculation (using the precise geometry of Au/TiO_2) produces approximately the same results for absorption of Au/TiO_2 nanocomposites (Figure 2). The width of the experimental absorption spectrum is larger although it has close peak position to the spectra obtained theoretically. Thus all spectra have Lorentzian shape predicted by Mie theory with the maximum corresponding to localized plasmon resonance (LPR) of Au nanoparticles in appropriate medium.
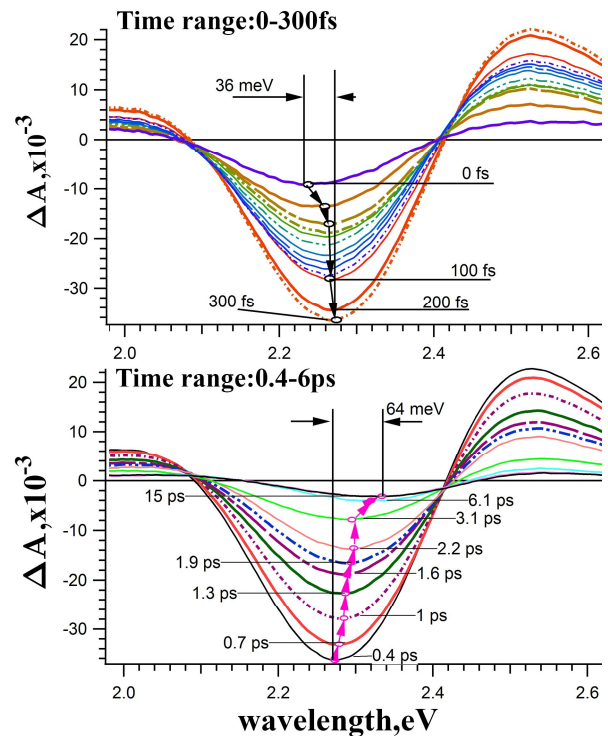
Figure 3: The evolution of differential absorption spectra in femtosecond pump-probe experiments.

Similarly, the time evolution of differential absorption spectra in pump-probe experiments can be describe as difference of the Lorentz terms:

$$\Delta A(\omega, t) \sim \left(\frac{\gamma(t)}{(\omega - \omega_0(t))^2 + \gamma^2(t)/4} - \frac{\gamma_0}{(\omega - \omega_0)^2 + \gamma_0^2/4} \right) \quad (1)$$

here $\gamma(t)$, γ_0 are the widths of the Lorentz shapes, while $\omega_0(t)$ and ω_0 are corresponding peaks. Typical shape of $\Delta A(\omega, t)$ is shown on Figure 3. The minimum of $\Delta A(\omega, t)$ (further, $\Omega(t)$) points to the instant LPR

position of investigating system. The shift of the $\Omega(t)$ toward the higher energies means that real position of LPR shifts to lower ones (which is result of (1)). For some systems (e.g. AuNP in water or chloroform) the position of $\Omega(t)$ does not have considerable shifts for all time delays in pump-probe experiment and approximately located at the LPR frequency (which can be found by Mie theory) of the system [10]. The time evolution of $\Delta A(\omega,t)$ for the mentioned systems can be described in terms of two temperature model [11] which takes into account the interaction of electron and phonon sub-systems. Transient dynamics of electron and phonon temperatures leads to evolution of $\gamma(t)$ in (1) which mainly reveal itself as the evolution of $\Omega(t)$ amplitude but does not have prominent effect on its position. Therefore this approach can not explain $\Delta A(\omega,t)$ evolution for Au/TiO$_2$ nanocomposites which is shown on Figure 3. The shift of 35 meV for $\Omega(t)$ was registered for time delays (0,300) fs (upper figure) and additional shift of 64 meV occurs for time delays up to 6 ps (lower figure).
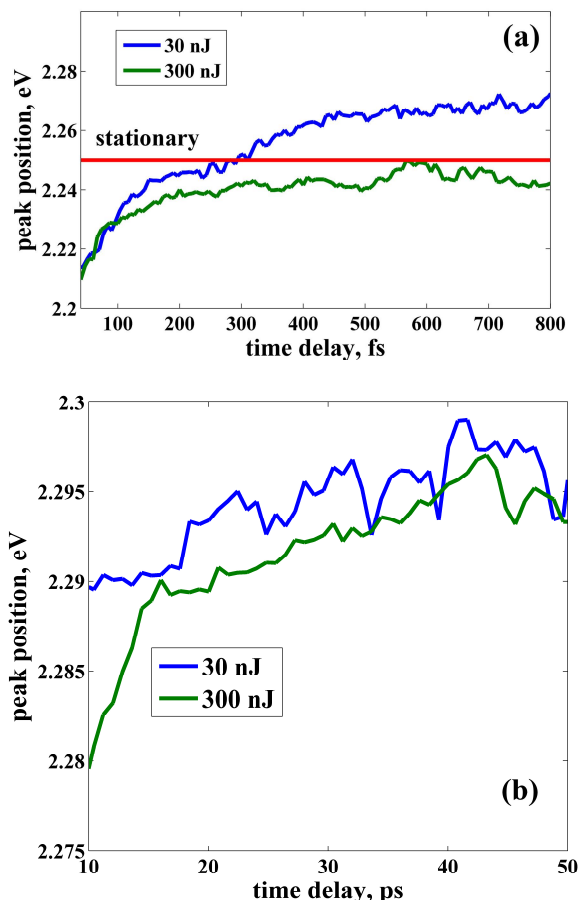

Figure 4: $\Omega(t)$ evolution for various pump powers.

Detailed time evolution of $\Omega(t)$ is shown on Figure 4(a,b). Taking into accoung that the stationary ($t \to \infty$) position of LPR (further Ω_0) of the system is at 2.25 eV

(Figure 2, red line of Figure 4a) it can be seen that $\Omega(t)$ blue shifted from Ω_0 for time delays up to 50 ps. From the other hand, $\Omega(t)$ is red shifted with respect to Ω_0 for initial time delays from 0 to 300 fs (30 nJ) and even longer for 300 nJ. Such a behavior cannot be explained in terms of Kerr effect which should produce blue shift of $\Omega(t)$ (and red shift for real transient LPR position). Moreover, the initial position (for ~30 fs) of $\Omega(t)$ is not dependent on power of the pump pulse (Figure 4a) which is also not typical for Kerr effect.

The possibility of ultrafast electron transfer from Au NP to TiO$_2$ under the visible light irradiation was reported in earlier works [12,13]. It was supposed that electron injection occurs faster than 240 fs [13]. Basing on this assumption let us to disscuss the results of Figure 4 and 5. First, from TD-DFT [14] calculations it is clearly seen from Figure 5 that negative charged AuNP has red shifted LPR, while positive charged reveals the blue shift. This means that $\Omega(t)$ would be red shifted for positive charged nanoparticles with respect to Ω_0. This is really the case shown in Figure 4a for time delays up to 300 fs (30nJ). Thus, in addition to [13] we could state that electron injection occurs for very initial times of order of 20-30 fs which shifts LPR position toward higher energies.
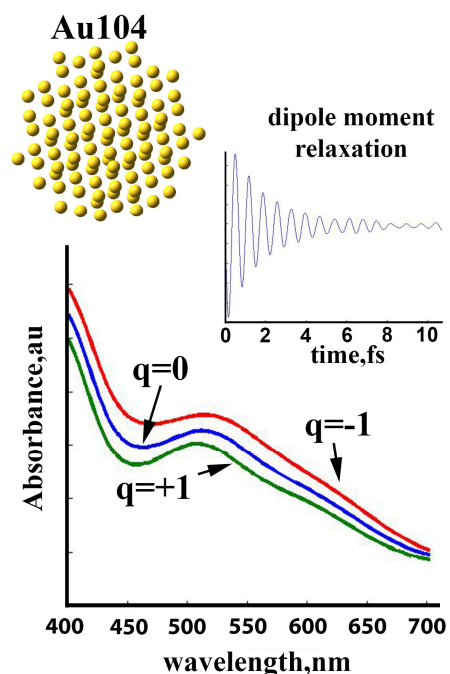

Figure 5: LPR shifts for charged AuNP.

The mechanism of electron injection can not have strong dependence on power of the pump pulse (like Kerr effect) since the fast grow of the ionization potential of metallic nanoparticles. Instead, the initial positions for $\Omega(t)$ are the same both 30 nJ and 300 nJ pump pulses

(Figure 4a). Moreover, for long time delays (of order of tens ps) the positions of $\Omega(t)$ are close to each other both for 30 and 300 nJ as opposite to imtermediate time delays (Figure 4b). This can be caused by injected electron relaxation (which is reasonably longer for 300nJ) in numerous traps of TiO_2. The trapped electron should increase dielectric permittivity of TiO_2 which must lead to the red shift of LPR and blue shuft for $\Omega(t)$ (Figure 4b). Since the number of initially injected electron is supposed the same for 30 and 300 nJ the final positions (~50 ps) of $\Omega(t)$ should be the same too.

ACKNOWLEDMENTS

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