Au/TiO$_2$ nanocomposites with high concentrated “hot spots” under near IR femtosecond pulsed excitation

A Aiboushev$^1$, A Astafiev$^1$, O M Sarkisov$^1$ and V A Nadtochenko$^{1,2}$

$^1$ N.N. Semenov Institute of Chemical Physics RAS, Moscow, Russia

$^2$ Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia

E-mail: aiboosh@gmail.com

**Abstract.** Luminescence of gold nanoparticles photodeposited on titan dioxide mesoporous films has been studied using multiphoton microscopy. Luminescence was registered under the two-photon excitation by femtosecond pulses of Ti:sapphire laser. It was observed that Au/TiO$_2$ mesoporous films have high concentration of bright luminescence spots (“hot spots”) which reveal stability to degradation under long illumination. The most intense “hot spots” have luminescence enhancement of order of $10^5$ therefore Au/TiO$_2$ nanocomposites can be useful for single molecule spectroscopy and biological objects visualization. Application of Au/TiO$_2$ mesoporous films for Raman scattering spectroscopy is demonstrated for the case of Rhodamine B. Au/TiO$_2$ geometry analysed with FDTD to find probable “hot spot” configurations.

1. Introduction

Mesoporous films, composed from TiO$_2$ nanoparticles can be used as a photocatalyst for conversion of light energy to chemical energy [1]. However the efficiency of photocatalytic reactions is limited by recombination processes and by absorption in visible [2]. Metal nanoparticles deposited on TiO$_2$ surface can essentially improve catalytic properties of TiO$_2$ [3]. Moreover enhancement of electromagnetic field near metallic nanoparticles could be the most important reason for dramatic increase of Raman scattering cross section or for luminescence spectroscopy enhancement [4-6]. Thus noble metal nanoparticles are very attractive since their localized surface plasmon resonance (LSPR) in visible.

The frequency of LSPR can be spectrally tuned by changing shape, dielectric environment of the particles and their size [7]. For complex shape particles, there can be several resonances corresponding to each polarization. The width of electromagnetic scattering and absorption wave resonance on metal particle is determined by surface plasmon damping. There are several damping mechanisms: radiative damping, one-electron energy relaxation and Landau damping in finite system [7-8]. These dampings lead to a decrease in the LSPR magnitude and near field intensity as well as to an increase of the LSPR width [9-10].

Clusters of noble metals can reveal photoluminescence in visible [11-12,16]. Surface roughness of clusters and impurities (e.g., oxides) can give a contribution to noble metal photoluminescence.

In the present work we report the effect of enhanced luminescence of gold nanoparticles (photodeposited on TiO$_2$ mesoporous film) under the two-photon excitation by femtosecond laser...
pulses of Ti:sapphire laser. We registered many bright luminescence spots in the film. To interpret experimental results different possible configurations of Au/TiO₂ nanoparticles were analyzed. Application of Au/TiO₂ mesoporous films for Raman scattering spectroscopy is demonstrated for the case of Rhodamine B.

2. Samples

Porous nanocrystalline TiO₂ electrodes were prepared from TiO₂ powder (Degussa P25), using the method similar to that described previously [13]. The powder, to which a small amount of water and acetyl acetone was added was milled for a prolonged time in order to lower the degree of aggregation. A white viscous paste was obtained, to which some nonionic detergent (Triton X-100) was added. Paste was deposited on glass microscope plate surface by “doctor blade” technique. Finally, the samples were heated in a furnace at 450 C (in air) for 2 h.

Au nanoparticles were obtained on the porous TiO₂ by the photodeposition technique: TiO₂ plate dipped in the solution 0.1 mM HAuCl₄ in water (ethanol concentration was 5%) and was illuminated by Philips phosphor lamp. The lamp has following characteristics: spectral range between 340 and 380nm, maximum of the spectrum is at 365nm, flux power 3mW/cm².

![Figure 1. SEM image of Au/TiO₂ mesoporous film for: (a) short deposition time (30 sec); (b) middle deposition time (4 min). (c) Absorption of Au nanoparticles photodeposited on TiO₂ mesoporous film for various deposition times (absorption of pure TiO₂ subtracted): 1) 4 min, 2) 8 min, 3) 15 min, 4) 25 min.](image)

SEM analysis (figure 1) of TiO₂/Au mesoporous film shows that the average size of TiO₂ nanoparticles is 30nm. Average size of Au nanoparticles and their distribution over TiO₂ mesoporous film depend on photodeposition time. For short deposition time (< 1 min) average size of Au nanoparticles was 5 nm. Photodeposition time on figure 1a was 30 sec. Single Au nanoparticles predominated over film surface. For long deposition time average size of Au nanoparticles was 20 nm. In this case both large Au nanoparticles (~50 nm) and nanoparticle agglomerates also were detected.
Au nanoparticles distribution over the film for middle deposition time can be characterized as following. First, single Au nanoparticles predominated over film surface. Second, there are coupled Au nanoparticles (surface concentration ~10^5 cm^-2) on the film (figure 1b). In this case distance between nanoparticles is less than nanoparticles size. Such configurations are discussed in section 5.

It is seen from SEM experiments that Au nanoparticles have the shape near to spherical (figure 1a,b). As it was mentioned in section 1 LSPR position (and absorption) of metal nanoparticles depends on nanoparticles shape. To obtain average absorption spectra of gold nanoparticles the same area of TiO_2 film was measured (by Shimadzu spectrophotometer) before photodeposition and after photodeposition of metal nanoparticles. The differential spectra revealed a plasmonic absorption peak, which was at about 540 nm (figure 1c). The magnitude of the peak increases with deposition time, but position and the shape remains approximately constant. According to FDTD analysis (see section 5) such absorption curves correspond to spherical Au nanoparticles with small contact area with TiO_2. It should be noted here that absorption measurements are not microscopic measurements therefore they have statistical sense, i.e. most of Au nanoparticles (but not all) have a small contact with TiO_2. Additionally, solutions absorption was measured after photodeposition of Au nanoparticles. It occurred that for long deposition (~10 min) times there are typical features on absorption curves which correspond to absorption of Au nanoparticles. This means that Au nanoparticles deposited on the film from appropriate solution, but not after photocatalytic process.

In this work middle time of photodeposition studied (figure 1b). The main features of middle time of photodeposition are: 1) average sizes of TiO_2 and Me nanoparticles were 30 nm and 20 nm, respectively; 2) Au nanoparticles on TiO_2 are not the result of deposition from solution but photocatalytic process; 3) Coupled Au nanoparticles detected over the Au/TiO_2 film.

3. Experimental Setup

We used a titanium sapphire Mai Tai HP (Spectra Physics) laser producing 100 fs pulses centered near 800 nm, with a repetition rate of 80 MHz and about 20 mW average power coupled with an inverted microscope (figure 2). The sample was on piezoelectric nano-positioning stage (NT MDT, Zelenograd) which allowed the sample to be scanned over a range of 30 µm in the x and y directions.

![Experimental setup of multi-photon microscope.](image)

All experiments were carried out using Olympus UPLSAPO 100× NA 1.40 apochromatic objective to focus laser beam onto the sample and collect emitted light, which was then imaged after
spectrograph SP-300i (Acton Research) by an electron multiplier CCD camera Newton EM (Andor). Luminescence spectra were measured in every points of scanning field. Laser scattered light in range 700-900 nm was cut by SWF-750-B filter.

Mai Tai HP laser was replaced by He:Ne laser for Raman scattering measurements. He:Ne laser produced continuous-wave radiation at 632.8 nm and 1.5 mW. Such laser wavelength allowed to avoid strong luminescence from Rhodamine B (since low absorption at this wavelength for Rhodamine B).

4. Computational method details
Finite difference time domain method (FDTD) of solving Maxwell equations was used to calculate nanoparticles extinction and electromagnetic field distribution. Quite traditional attributes of FDTD such as PML (perfect match layer), periodic boundary conditions, TFSF method, frequency dispersion of metal dielectric permittivity were implemented in the program code and used in calculations [14-15]. Dielectric functions of TiO$_2$, Ag and Au were taken from SOPRA web site. Throughout the calculations x, y, z mesh steps were 0.25 nm for precise description of such geometrical features as the gap between nanoparticles etc.

5. Results and discussion
An example of the luminescence scan of Au/TiO$_2$ mesoporous film represented on figure 3a. Wavelength of excitation $\lambda_e$ was 825 nm. It is seen that the image consists of a large number of bright spots in which the signal intensity substantially exceeds the background level. The size of such “hot spot” with bright luminescence was ~300 nm (the size of one pixel is 160nm), roughly coinciding with the limit of spatial resolution of the microscope. Spectra in various pixels of the film (circle centers on figure 3a) are shown on figure 3b. Both bright and dark spots of the film have broad luminescence spectra ranging from ~400 to ~800nm. As it was mentioned in section 3 the upper limit (800 nm) is the result of applied filter. But the lower limit coincides with $\lambda_e/2$ (second harmonic). Moreover second harmonic is pronounced for “hot spots” of the film (curves 1, 2, 3 on figure 3b). Investigation of signal level for various laser pulse power also showed second order of non-linearity. Thus a conclusion can be made: the luminescence signal observed in experiments is two-photon luminescence. The intensity ratio between (for example, between curve 2 and curve 5 on figure 3b) the most intense and dark pixels of the film is ~7.

Figure 3. (a) Hot spots distribution in two-photon microscopy scan of Au/TiO$_2$ mesoporous film, (b) photoluminescence spectra in various pixels of the film. Excitation wavelength $\lambda_e = 825$ nm, scanning area size 10×10 $\mu m$. 

[Image of Figure 3]
The concentration of “hot spots” in two-photon experiment (figure 3a) is considerably lower than metal particle concentration on TiO₂ mesoporous film (figure 1a). Therefore some specific configurations of nanoparticles on the film exist which the most effectively enhance electromagnetic field to form the “hot spot” in luminescence experiment. Two types of measurements were made to reveal additional properties of “hot spots” of Au/TiO₂ films.

**Figure 4.** Dependence of integral luminescence intensity of “hot spots” of Au-TiO₂ mesoporous film on: (a) excitation wavelength; (b) direction of linear polarization of excitation laser pulse.

First, the dependence of integral luminescence of “hot spots” on laser excitation wavelength was measured (figure 4a). As can be seen from figure 4a the “hot spots” integral luminescence decreases for longer excitation wavelengths $\lambda$ in experiment. Second, the influence of the direction of linear polarization of incident laser pulse on the integral luminescence in “hot spots” was studied. The dependence of the integral luminescence on various polarization directions (angles with respect to initial direction of pulse polarization) represented on figure 4b. As can seen from figure 4b there is only one pronounced maximum for each “hot spot” of the film.

**Figure 5.** FDTD calculation: (a) electromagnetic field distribution in Au/TiO₂ model system; (b) normalized absorption of two Au spherical nanoparticles in vacuum environment (radius 10 nm, distance between particles 2 nm): 1) p-polarization, 2) 45 degrees between system axis and light polarization, 3) s-polarization, 4) p-polarization, spheres placed on TiO₂ surface.

The electromagnetic field transformation in Au/TiO₂ film could be divided on three main stages. First stage is local electromagnetic field enhancement (EFE) $\alpha$ at $\lambda$ (wavelength of excitation in experiment). Second, two-photon absorption at $\lambda$. Third, two-photon luminescence of the
mesoporous film (figure 3b). Therefore bright spots (“hot spots”) with enhanced two-photon luminescence of Au/TiO$_2$ film should be result of EFE at $\lambda_c$. Moreover, two-photon luminescence enhancement is proportional to $\alpha^4$.

Figure 5a represents the result of FDTD calculation of electromagnetic field distribution for Au spherical nanoparticles on TiO$_2$ substrate. It is seen several configurations from figure 5a which have enhanced electromagnetic field (lightened areas). Areas labeled by 1 represent typical Mie distribution for single spherical particle. “Hot-spots” of Au/TiO$_2$ can not be explained by such areas by following reasons. First, in this case “hot-spots” concentration should be approximately the same as particle concentration but it is not. Second, such areas do not have some specific axis to reveal the dependence similar to figure 4b.

Areas labeled by 2 show EFE in the gap between two coupled nanoparticles (dimer). Calculation of absorption spectra for Au coupled nanoparticles (dimer) for various angle between dimer axis and direction of linear polarization represented on figure 5b. It is seen from figure 5b that distance between LSPR position (and absorption peak) and $\lambda_c$ is minimal for p-polarization. Therefore such a system has maximum EFE $\alpha$ for p-polarization, i.e. single maximum for all range of angles. The same behavior was observed in figure 4b. On the one hand, according to SEM results the shape of Au nanoparticles is close to spherical (see section 2), i.e. figure 4b can not be explained by EFE $\alpha$ of single Au nanoparticles. From the other hand, the dimer of nanoparticles is the simplest configuration which can explain experimental data represented on figure 4a and figure 4b.

Figure 5b and figure 6a show the influence of TiO$_2$ substrate on absorption of Au/TiO$_2$ nanocomposites. It is seen from figure 5b that even small contact with TiO$_2$ for dimer of Au nanoparticles lead high absorption at $\lambda_c$. From the other hand, figure 6a shows that absorption maximum of Au spherical particle on TiO$_2$ shifts from 550 nm to 665 nm while particle imbedding from 0 nm to 10 nm. Also the imbedding leads to rise of absorption, particularly at $\lambda_c$.

It was noted in section 2 that Au nanoparticles formed on TiO$_2$ surface by photocatalytic process. This means that actually Au nanoparticles are cut by TiO$_2$ surface. Figure 6a shows absorption spectrum for such cut dimer of Au spherical nanoparticles ($r = 10$ nm). It occurs that when distance...
between nanoparticles is 2nm absorption peak is at 770nm which is very close to $\lambda_e$. Moreover, absorption curve has only one pronounced maximum and decreases for wavelength longer than 770 nm. This is also in accordance with figure 4a, i.e. such a system should reveal decrease in integral luminescence for wavelength longer than $\lambda_e$ (825 nm). Thus, nanoparticles dimer shown on figure 6a should lead near to the highest luminescence enhancement in “hot-spots” of Au/TiO$_2$ film. Considering this system as ideal configuration let us estimate real “hot-spot” luminescence enhancement. On the one hand, resolution in two-photon experiments was ~300 nm (see above). On the other hand, the most intense electromagnetic field concentrated in the gap between nanoparticles (figure 6a). Taking into account that luminescence enhancement in two-photon experiments was ~7 one can obtain the luminescence enhancement in the gap should be of order of $10^5$. Corresponding EFE $\alpha$ should be $\approx 20$.

In conclusion a Raman scattering signal was observed for Rhodamine B molecules deposited on Au-TiO$_2$ film surface. Figure 6b represents a spectrum of signal detected (intensity vs. Raman shift). The position of Raman peaks was in good agreement with the one observed in [17,18]. At the same time no appreciable signal was observed for Rhodamine B molecules on the surface of pure TiO$_2$ film. Au/TiO$_2$ nanocomposites show promising application not only for Raman scattering spectroscopy but also for biological objects visualization. This is because of high “hot spots” concentration over the TiO$_2$ surface ($\sim 10^5$ cm$^{-2}$) and large EFE $\alpha$ of “hot spots” in near IR ($\sim \lambda_e$).

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7. References
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