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Femtosecond Ti:sapphire Laser Pulses to Deposit Precious Metal Nanoparticles on Crystalline and Amorphous Titanium Dioxide Films

In the present work we report the effect of enhanced luminescence of gold and silver nanoparticles photodeposited on crystalline and amorphous films of TiO₂. Such a system has two main characteristic features. The average distance between metal nanoparticles is of order of several nm. Metal nanoparticles size is less than (or of order of) 10nm. Absorption spectra of the mesoporous films additionally show that most of metal nanoparticles have approximately spherical shape.

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1. Introduction

It is becoming apparent that nature's bottom-up approach to functional nanostructures can be mimicked to produce artificial molecules with nanoscaled dimensions and engineered properties [1]. Indeed, examples of artificial nanohelices, nanotubes, and molecular motors are starting to be developed [2]. Some of these fascinating chemical systems have intriguing electrochemical and photochemical properties that can be exploited to manipulate chemical, electrical, and optical signals at the molecular level [3]. This tremendous opportunity has led to the development of the molecular equivalent of conventional logic gates. Simple logic operations, for example, can be reproduced with collections of molecules operating in solution [4]. However, most of these chemical systems are based on bulk addressing to execute both combinational and sequential logic operations [5].

The constituent components of conventional devices are carved out of larger materials relying on physical methods. This top-down approach to engineered building blocks becomes increasingly challenging as the dimensions of the target structures approach the nanoscale [6]. Nature, on the other hand, relies on chemical strategies to assemble nanoscaled biomolecules [7]. Small molecular building

blocks are joined to produce micro and nanostructures with defined geometries and specific functions [8].

The 'newness' of the nanoscale refers to the difference between the macroscopic and nanoscopic properties of materials [9]. Although a metric ton, a kilogram, and gram of gold or silver all have the same physical properties, the same is not true when one scales down to the nano length [10]. Gold's and silver's color, melting point, and chemical properties are different at the nano length scale as a result of the nature of atomic interactions and the fact that these are not averaged out as they are in bulk material. In other words, nano gold and silver don't act like bulk gold and silver [11].

Novel biosensors based on optical properties of gold and silver nanoparticles have been reported [12]. There have been numerous reports in recent years on similar sensors also based on localized surface plasmon resonance of gold and silver nanoparticles [13]. Advantages cited for these sensors over other sensors are simplicity of the instrument, low costs, ability to give a result that can be read off visually, etc [14-16]. On the other hand, there have been few reports on the actual performance [17]. It has been observed that the dependence of the peak wavelength on the refractive index of the surrounding material is

significantly lower, by more than one order of magnitude [18]. Similar observations were made but as far as detection of biomolecules is concerned, it has a sensitivity significantly higher than what the result of the bulk dependence leads one to believe [19].

Hybridization confirms that the analyte is present; finding out whether hybridization has occurred isn't trivial [20]. We can't see the double strands without very sophisticated instruments; consequently, the determination is usually made by mass [21]. Obviously double strands have a greater mass than single strands, though it may not be by much if the test sequence is short since each base pair weighs only as much as a molecule or roughly 10^{-21} of a gram [22]. This is much too small to measure easily in any direct way, so it is necessary to amplify the response before it can be measured [23]. One of the great challenges of DNA sensing is therefore to amplify the effects of hybridization so that they can be easily measured [24]. One way to provide this amplification is to change the optical properties of gold or silver nanodots that are attached (technically "functionalized") to the DNA [25]. The combination of quantum optical effects (remember the changes in the color of gold upon changing the size of the gold clusters) and molecular recognition (complementary DNA binding) were reported [26,27].

Mesoporous films, composed from titanium dioxide (TiO_2) nanoparticles can be used as a photocatalyst for conversion of light energy to chemical energy [28,29]. Metal nanoparticles deposited on titanium dioxide (TiO_2) surface can essentially improve catalytic properties of titanium dioxide (TiO_2) [30,31]. Moreover enhancement of electromagnetic field near metallic nanoparticles could be the most important reason for dramatic increase of Raman scattering cross section or for enhancement in luminescence spectroscopy [32,33].

In the present work, we report the effect of enhanced luminescence of gold and silver nanoparticles photodeposited on crystalline and amorphous films of titanium dioxide (TiO_2). Such a system (shown in Fig. 1) has two main characteristic features. First, the average distance between metal (Au and Ag) nanoparticles is of order of several nm. Second, metal nanoparticles size is less than (or of order of) 10 nm (Fig. 2a). Absorption spectra of the mesoporous films additionally show that most of metal nanoparticles have approximately spherical shape (Fig. 2b, 4b). The tiny gold nanostructures that we prepared are sometimes called *quantum dots* or *nanodots* because they are roughly dot-shaped and have diameters at the nanoscale.

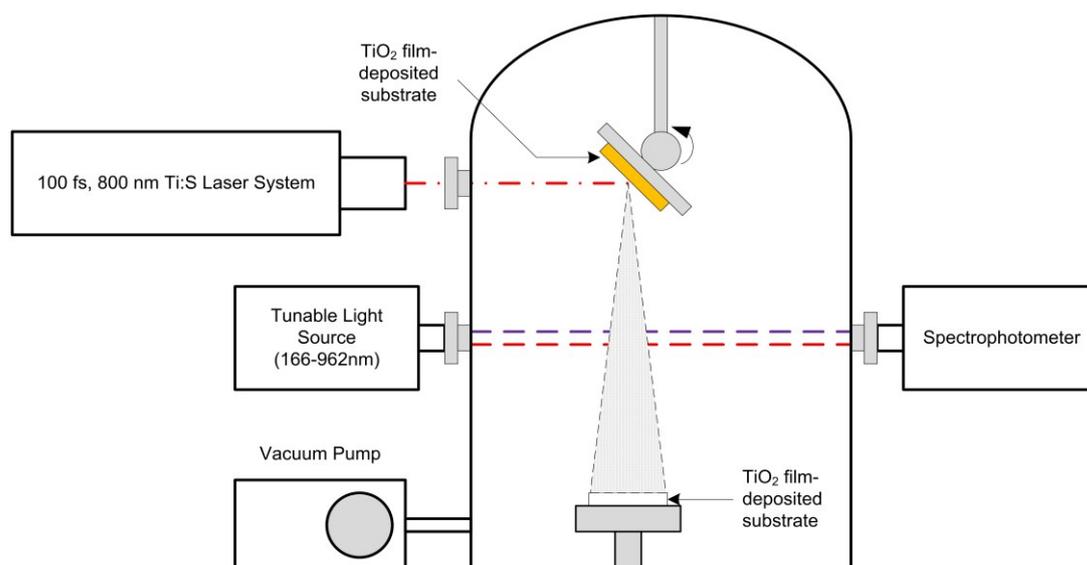


Fig. (1) Experimental setup used in this work

2. Experiment

Luminescence was registered under the two-photon excitation by femtosecond pulses (100fs, 800nm) of Ti:sapphire laser. It occurs that Ag/TiO₂ and Au/TiO₂ mesoporous films have high concentration of bright luminescence points which reveal stability to degradation under long illumination [34,35] (Fig. 3a). The luminescence of Me-TiO₂ films is in the range from 400nm to ~750nm (Fig. 3b).

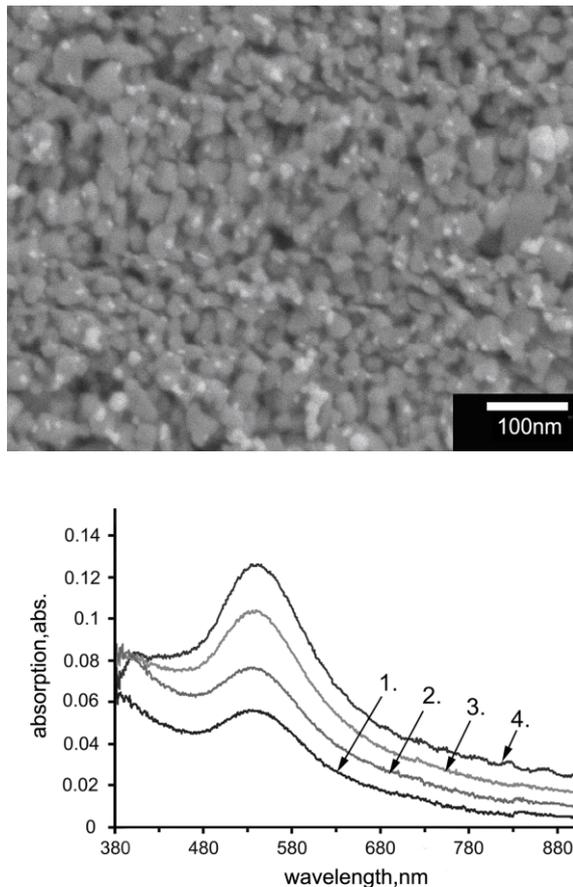


Fig. (2) (a) SEM image of the Me/TiO₂ mesoporous film, (b) experimental absorption spectra of the mesoporous films with various times of nanoparticle deposition: (1) 4 min (2) 8 min (3) 15 min (4) 25 min

Clusters of noble metals can reveal photoluminescence in visible. Surface roughness of clusters and impurities (e.g., oxides) can give a contribution to noble metal photoluminescence. After comparison with luminescence of pure Au and Ag nanoparticles following conclusion was made: the main contribution to the luminescence of Me/TiO₂ mesoporous films is the luminescence of metal nanoparticles.

It is essential to devise methods to reproduce these useful functions in solid-state

configurations and, eventually, with single molecules. These challenging objectives are stimulating the design of clever devices that interface small assemblies of organic molecules with macroscaled and nanoscaled electrodes. These strategies have already produced rudimentary examples of diodes, switches, and transistors based on functional molecular components. The rapid and continuous progress of this exploratory research will, we hope, lead to an entire generation of molecule-based devices that might ultimately find useful applications in a variety of fields, ranging from biomedical research to information technology.

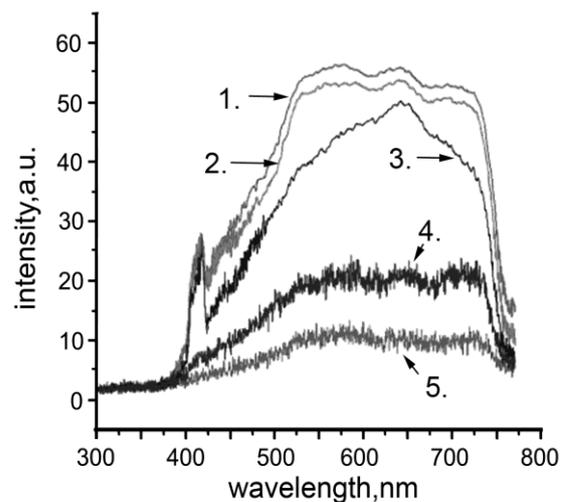


Fig. (3) Luminescence spectra from various pixels of the Au/TiO₂ mesoporous film in two-photon microscopy experiment

Since metallic particles are distributed rather uniformly over the mesoporous film, some specific configurations of nanoparticles in the film exist which the most effectively enhance electromagnetic field to form the “hot spot” in luminescence experiment. The most intense electromagnetic field concentrates in region between nanoparticles and strongly depends on distance between nanoparticles. Assumption can be made that the majority of “hot spots” of Me/TiO₂ mesoporous films caused by coupled metallic nanoparticles. Therefore the size of localization of the most intense electromagnetic field is of order of distance between nanoparticles. Since that the luminescence enhancement of “hot spot” in two-photon microscopy experiment is estimated as 10^4 .

On the other hand, the effect of two-photon absorption and subsequent luminescence is proportional to E^4 , where E is the amplitude of

electromagnetic field at wavelength of the excitation. Therefore enhancement of “hot spot” field at wavelength of the excitation (800nm) should be $\approx \sqrt[4]{10^4} = 10$. Such enhancement coefficients can be easily achieved using metal nanoparticles deposited on TiO₂ mesoporous films [36,37].

Owing to the potential applications in electrical and optoelectronic devices, titanium oxide (TiO₂) has recently attracted intense theoretical and experimental attention. TiO₂ is a metallic oxide semiconductor of which the optical band gap varies depending on the preparation method and substrate type. Controlling the deposition conditions of titanium dioxide (TiO₂) films is an important step in controlling their electrical properties, facilitating the device design. Apart from the optical properties, it is of crucial importance to understand the charge transport processes in titanium dioxide (TiO₂).

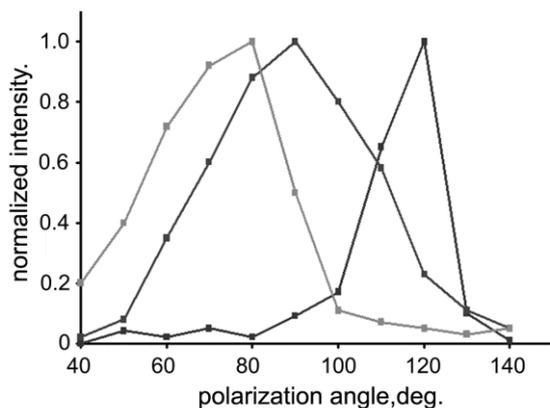


Fig. (4) Integral intensity of “hot spots” luminescence with various polarization of laser pulse

Luminescence intensity reveals “hot spots” dependence on the polarization of excitation laser pulse (Fig. 4). The model of two coupled Me nanoparticles (dimer) can explain such a behavior (Fig. 5). Moreover, investigating various metal nanoparticle geometries on TiO₂ it occurs that the system of two coupled metal nanoparticles is the most preferable for the explanation of “hot spots” on Me/TiO₂ mesoporous films.

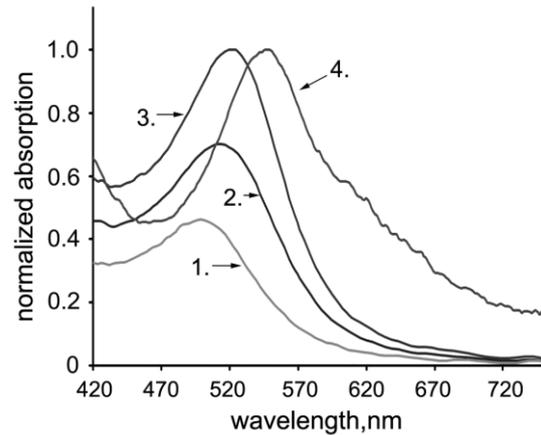


Fig. (5) Absorption spectra (FDTD result) of Au sphere dimer (radius 10nm, distance 2nm) with various polarization of incident light: (1) s-polarization (2) 45° between dimer axis and E (3) p-polarization (4) Au dimer on TiO₂ surface

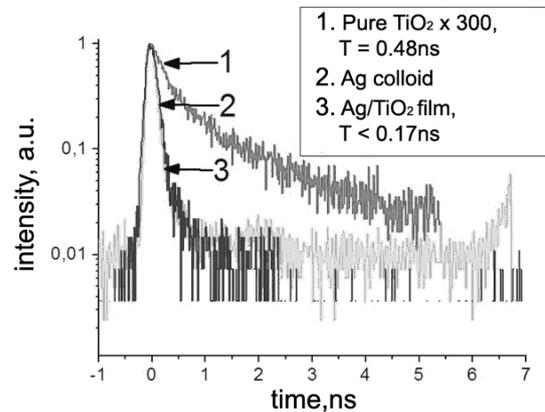


Fig. (6) Kinetic curves of luminescence of pure TiO₂, Ag colloid and Ag/TiO₂ mesoporous film

Kinetic properties of Me/TiO₂ mesoporous films were studied in two-photon microscopy (resolution 100ps) and femtosecond transient absorption spectroscopy (pump-probe; resolution 10fs) experiments. Such techniques allowed to find luminescence decay times of pure TiO₂ and Me/TiO₂ mesoporous films; electron gas thermalization in Me nanoparticles; to investigate the process of electron injection from metal nanoparticles to TiO₂ conductive band (Fig. 6 and 7). TD-DFT method was used to investigate decay times of collective oscillations of electrons in Au and Ag nanoclusters.

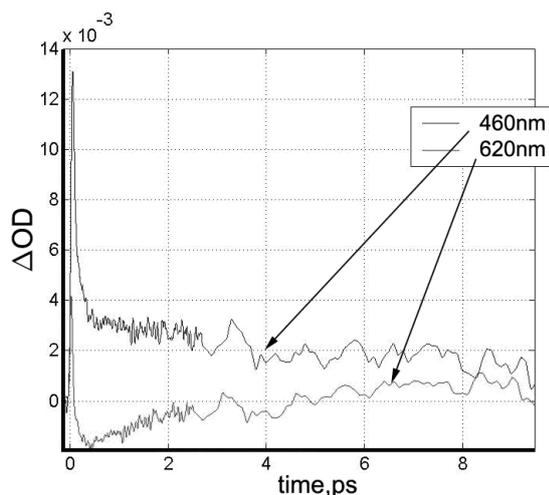


Fig. (7) Au/TiO₂ mesoporous film relaxation in pump-probe experiment of femtosecond spectroscopy

Conclusion

The effect of enhanced luminescence of gold and silver nanoparticles photodeposited on crystalline and amorphous films of TiO₂ was reported. Such a system has two main characteristic features. The average distance between metal nanoparticles is of order of several nm. Metal nanoparticles size is less than (or of order of) 10nm. Absorption spectra of the mesoporous films additionally show that most of metal nanoparticles have approximately spherical shape. The Au/TiO₂ system can be useful for single molecule spectroscopy and visualization of biological objects. Application of Me/TiO₂ mesoporous films for Raman scattering spectroscopy is demonstrated for the case of Rhodamine B.

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