



## Two-photon luminescence enhancement of silver nanoclusters photodeposited onto mesoporous TiO<sub>2</sub> film

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### ABSTRACT

We report on two-photon luminescence of silver nanoparticles grown on non-crystalline mesoporous TiO<sub>2</sub> issued of the sol–gel process. The growth is achieved by surface photocatalytic reduction from silver nitrate solution. A structural hierarchy of this particular TiO<sub>2</sub> system results in a characteristic distance between nanoparticles ~10–100 nm that is optimal for the electromagnetic field enhancement. The microscope images evidence multiple bright luminescence spots at two-photon near-IR femtosecond laser excitation due to the field enhancement effect. The spectra suggest homogeneous size distribution of emitting silver clusters over the sample area on the scale below 100 nm.

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### 1. Introduction

Electromagnetic field (EF) enhancement on rough metals is of continuous interest since first work by Fleischmann et al. [1]. It is now known that this effect is due to the surface plasmon localization [2,3] creating hot spots or regions with giant EF resonance. The relevant multiple-scattering process, strongly promoted by nanoscale surface roughening, enables surface-enhanced spectroscopies [4] of extremely high sensitivity: surface-enhanced Raman scattering [5], luminescence [6], second harmonic generation [7] and multiphoton photoemission [8].

The related phenomena are recognized as highly heterogeneous with arbitrary EF enhancements at different hot spots. Two classes of systems are expected to favour such sites: (i) small metallic nanoparticles in form of dimers, trimers, and larger aggregates, in which EF maximum is attained at interstitial sites, and (ii) large fractal aggregates in which the hot spots arise from the scaling symmetry breakage by excitation [9]. The major weight of experimental evidence of that points to the fact that it is these hot spots that are responsible for the major part of the giant enhancements that can attain  $\sim 10^{14}$  as reported by many research teams [10,11]. This EF enhancement appears to be high enough to allow almost routine detection of Raman and fluorescence spectra of isolated molecules.

Adequate sample preparation and roughness control are critical for observation of the EM enhancement effect. Recently, we have

demonstrated an interesting approach to amorphous photocatalyst preparation based on oxo-alkoxy cluster activity [12,13]. These species produce open structures with high specific surface (BET)  $\sim 450$  m<sup>2</sup>/g and interstitial sites distances in the range ~10–100 nm, that is favourable for plasmon effects observation. As no thermal treatment is applied, the pristine material morphology conserves during the elaboration process. Moreover, photocatalytic character of TiO<sub>2</sub> permits growing of silver clusters directly on titania surface. We remark that similar silver growth on crystalline anatase TiO<sub>2</sub>, which is known as an excellent photocatalyst, is expected to result in samples with much lower specific surface.

The present work reports on first preparation of silver clusters on precipitated non-crystalline TiO<sub>2</sub> sol nanoparticles and observation of their surface enhanced luminescence. The local maximums of EF were observed by their bright luminescence under two-photon excitation by femtosecond Ti:Sapphire laser. The considered Ag<sub>N</sub>/TiO<sub>2</sub> system allows reproducible fabrication of high-density hot geometries.

### 2. Experiment and sample preparation

#### 2.1. Sample preparation

The TiO<sub>2</sub> powder was prepared in a sol–gel reactor [14] using titanium tetraisopropoxide (Ti(OPr<sup>i</sup>)<sub>4</sub> or TTIP) as metal oxide precursor at concentration of 0.146 M and hydrolysis ratio  $H = [H_2O]/[TTIP] = 2.46$ . The chemicals undergo turbulent mixing in 2-propanol solution before react. Highly reactive TiO<sub>2</sub> colloids are maintained in the thermostated bath at 20.0 °C during the induction period of  $50 \pm 2$  min, at the end of which they are precip-

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itated. During induction period the sol particles slowly aggregate into low-dimension fractal structures ( $D \approx 1.4$ ). At precipitation, these fractals particles agglomerate into larger-hierarchy particles conserving their large specific surface inherent to constituting nanometric sols. The basic sol particles are non-crystalline, possessing inorganic titanium oxide core and surface propoxy and hydroxy groups. The precipitates were subjected to drying at 80 °C, which guarantees that no changes in chemical composition and morphology of the sample take place [12]. A thin pellet then was compacted from the TiO<sub>2</sub> precipitate by a simple mechanical press.

For silver cluster deposition we make use of TiO<sub>2</sub> photocatalytic activity. The relevant process in the crystalline TiO<sub>2</sub> involves the photoexcited electron transfer to the surface-bound Ag<sup>+</sup>, initiating cycles of alternating reduction and ion adsorption that make grow Ag particles [15] with a relatively high quantum yield of 3–10% [16]. Earlier studies showed that their size distribution in these conditions is relatively uniform and independent on irradiation time.

In our silver deposition, the TiO<sub>2</sub> pellet was dipped in the solution of 0.1 mM AgNO<sub>3</sub> in H<sub>2</sub>O:EtOH = 90:10 (volume partial). The surface of the pellet was exposed to 500 W Hg lamp radiation through the UV-filter with non-zero transmission in UV spectral range between 320 and 400 nm. The UV-power density on the sample surface was  $\sim 100$  mW/cm<sup>2</sup>. The irradiation time was varied from 10 to 30 min. In control blank experiment silver clusters were deposited on photocatalytically inert substrate (Al<sub>2</sub>O<sub>3</sub>) in similar conditions of UV-irradiation and solution composition. A very slow formation of silver colloid in the solution bulk by a direct photolysis was observed. The deposition rate of the colloid onto the Al<sub>2</sub>O<sub>3</sub> surface was more than an order of magnitude slower than that due to photocatalytic growth on the TiO<sub>2</sub> surface. As a consequence, participation of the direct photolysis in surface growth of silver clusters was disregarded as a minor reaction channel in our experimental conditions.

TTIP of 98% purity, AgNO<sub>3</sub> (Aldrich), 2-propanol (Interchim), ethanol (HPLC grade), and distilled water were used in current experiments.

## 2.2. Optical measurements

UV–visible diffuse reflectance spectra of TiO<sub>2</sub> pellet were measured with Specord M40 spectrophotometer. The Kubelka-Munk

relations were used to convert the reflectance ( $R$ ) measurements into equivalent absorption  $K$  and scattering  $S$  coefficients of TiO<sub>2</sub> according to Eq. (1). The MgO reflectance ( $R_{\text{MgO}}$ ) was used as the reference.

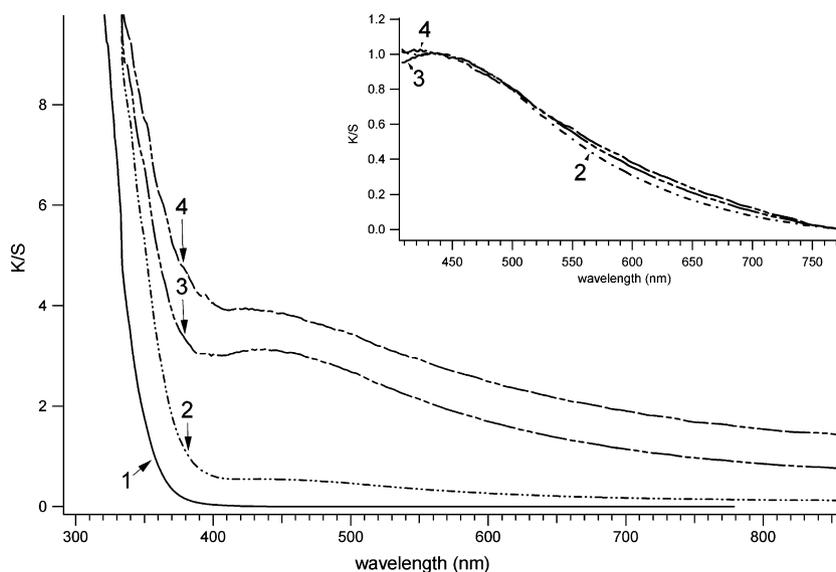
$$R_{\infty}(\lambda) = \frac{R(\lambda)}{R_{\text{MgO}}(\lambda)} \quad (1)$$

$$\frac{K(\lambda)}{S(\lambda)} = \frac{(1 - R_{\infty}(\lambda))^2}{2 \cdot R_{\infty}(\lambda)}$$

The sample luminescence was excited by Ti:sapphire laser Mai Tai HP (Spectra Physics) that delivers 100 fs pulses at  $\lambda = 800$  nm with repetition rate of 80 MHz and mean power of 20 mW. The laser radiation impacts samples being passed through an inverted microscope installation. The sample is mounted on a piezoelectric nanopositioning stage (NT MDT, Zelenograd), which allowed displacement in the  $x$  and  $y$  directions over a distance  $\sim 30$   $\mu\text{m}$ . All experiments were carried out using Olympus UPLSAPO 100  $\times$  NA 1.40 apochromatic objective that allows focusing laser beam onto the sample and collecting the emitted light. The sample images were recorded after SP-300i spectrograph (Acton Research) by CCD camera Newton EM (Andor). The luminescence spectra were measured in every point of the scanned image. An intense scattered laser light was suppressed by SWF-750-B filter.

## 3. Results and discussion

The absorption of the TiO<sub>2</sub> sol nanoparticles sets up at  $\lambda < 380$  nm in agreement with Soloviev et al. [17] who showed that the fundamental absorption onset of the oxo-alkoxy TiO<sub>2</sub> nanoparticles is blue-shifted respectively to that of the common nanocrystalline TiO<sub>2</sub> polymorphs. It is widely accepted that the photocatalytic activity of this phase is negligible because of bulk recombination sites, capable attracting both photoinduced charges [18]. However, the photocatalytic activity of the immobilized nanoparticles ( $2R = 5.2$  nm) strongly increases presumably due to a short transport distance and coupling to surface active sites [12,13]. In particular, 360 nm photons activate of these nanocoatings. Moreover, supported multiplayer 5 nm particles exhibit similar activity to that of the monolayer ones, which suggests either outer- or intra-layer activity.



**Fig. 1.** Kubelka-Munk functions  $K/S$  vs. wavelength for samples: pristine TiO<sub>2</sub> (1) and TiO<sub>2</sub> with deposited silver clusters after 5 min (2), 10 min (3), and 20 min (4) of UV-irradiation. Inset: normalized plasmon band of silver nanoparticles in (2–4).

Our results evidence silver clusters growth on oxo-alkoxy  $\text{TiO}_2$  particles. Fig. 1 shows diffuse reflectance spectra of  $\text{TiO}_2$  pellet after UV-illumination in the range of fundamental material absorption (320–380 nm). With an increase of the exposition time we observed the growth of a broad absorption band with the maximum at 450 nm assigned to plasmon. This band is strongly shifted compared to that in free clusters (340 nm). The shift has been earlier observed in silver clusters deposited/embedded onto silica substrate (to 400 nm) [19] and embedded into MgO matrix (to 540 nm) [20]. For this reason we attribute the observed shift to a particular cluster  $\text{Ag}_N\text{-TiO}_2$  interaction. Moreover, this band seems considerably broader in comparison with that generally observed. This particularity may be related to a small size and large distribution of most abundant silver clusters. The ability of oxo-alkoxy  $\text{TiO}_2$  particles to trap and deliver photoinduced charges, inducing surface redox reactions, is then confirmed in agreement with our earlier results [12,13].

The surface plasmon resonance was theoretically introduced by Mie for explanation of optical extinction of small spherical metal particles [21]. In general, the spectra are sensitive to the particle size and shape [22,23]. In framework of the Drude model the size-dependent dielectric function explains the observed  $1/r$  dependence of the plasmon bandwidth. In particular, the growth of deposited silver clusters (generally accompanying thermal treatment) results in a strong plasmon band narrowing [24]. However, according to our measurements (see inset in Fig. 1) the shape of the plasmon band is not sensitive to the irradiation time, whereas its intensity significantly increases with the time increase. This feature suggests that absorbance grows as a consequence of an increase of the number density of silver clusters rather than their size and/or shape changes.

A SEM image of the substrate is shown in Fig. 2a. The compacted pellet is composed of chains of relatively large 100 nm  $\text{TiO}_2$  particles. The basic unit of these particles is 5 nm nuclei formed in the beginning of the induction period [25], which escapes observations because of its small size. This precipitate conserves a high specific surface inherent to elementary particles that form an open structure [12,13]. The image of the pellet after the silver deposition is shown in the inset of Fig. 2a. At this stage the surface of  $\text{TiO}_2$  chains of 100 nm particles is found covered by silver clusters and nanoparticles of a mean size  $\bar{D} \approx 15$  nm. However, the particles smaller than 5 nm may not be counted in the statistics because of their negligible contrast. For this reason, the above  $\bar{D}$  value would better be called the most expected size. To guess about the presence of smallest silver particles, we analysed the size distribution accessed from the recorded SEM images. The obtained histogram appeared to be non-gaussian and close to the exponential decay  $f(D) \propto e^{-D/\bar{D}}$  with  $\bar{D} = 15 \pm 5$  nm. This result indicates that the most abundant particles corresponding of the maximum of  $f(D)$  are very small indeed.

Fig. 2b shows a typical microscope image of the fs near-IR laser-excited luminescence of the  $\text{Ag}_N/\text{TiO}_2$  sample. Multiple bright points are seen in the image at the dark background implying the presence of hot spots with giant EF: optical transition probability locally enhances in these areas. We remark that the number of these bright points initially increases with the exposition time or light dose. Moreover as the inset in Fig. 2b shows, their number density is generally higher than that observed in samples with silver deposition on crystalline  $\text{TiO}_2$  [26]. This observation is consistent with a large nanoporosity of non-calcinated  $\text{TiO}_2$  alcogel samples. We assign the observed luminescence to small silver clusters located in interstitial sites of large silver nanoparticles.

In fact, luminescence is typical for metal clusters, whereas non-radiative relaxation dominates in bulk metals. Small silver clusters are known to demonstrate multicolor emission depending on size [27]. It originates from all-electron excited states with radiative

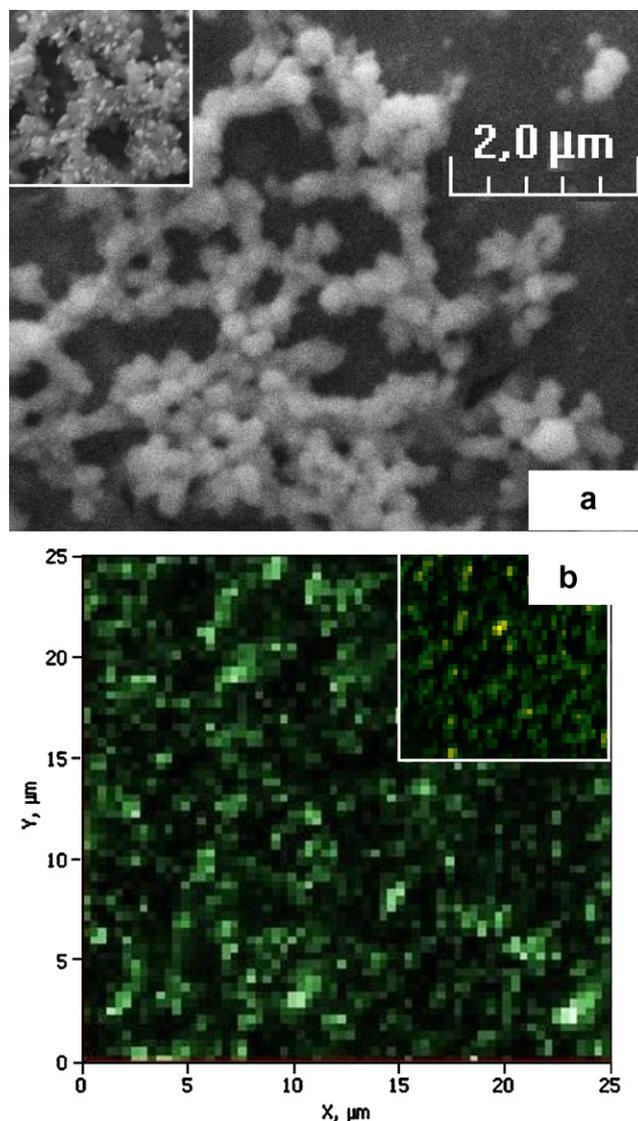
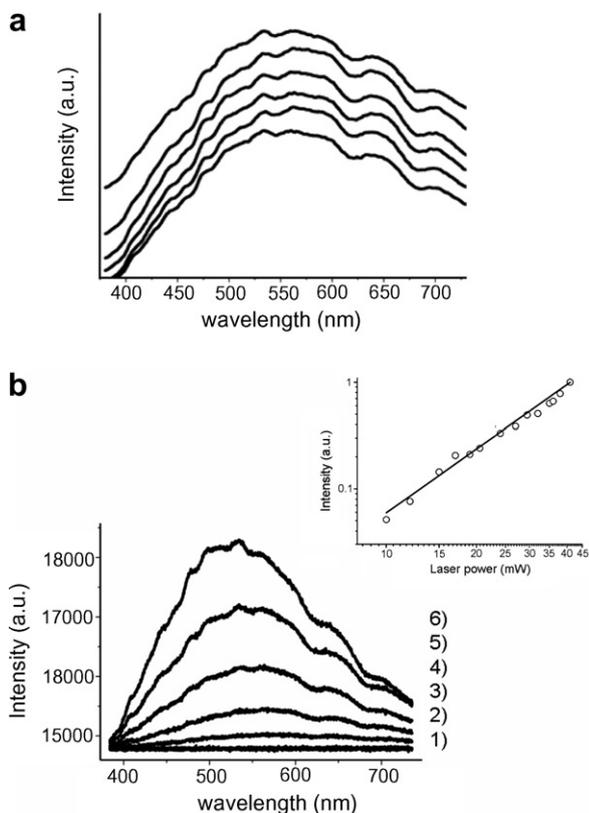


Fig. 2. SEM image of the  $\text{TiO}_2$  sample (a) and luminescence image of silver nanoparticles photodeposited on  $\text{TiO}_2$  ( $P_L = 15$  mW) (b). SEM image of  $\text{Ag}_N/\text{TiO}_2$  is shown in the inset of (a). Luminescence image of  $\text{Ag}_N$  deposited on anatase  $\text{TiO}_2$  is shown in the inset of (b).

lifetime typical of dipole-allowed electronic transitions: 0.1–10 ns [28]. In particular, strong luminescent species are oligomeric clusters  $\text{Ag}_N$  ( $N = 1\text{--}8$ ), which spectra cover UV–visible spectral range [26–29].

The luminescence properties of our  $\text{Ag}_N/\text{TiO}_2$  samples are presented in Fig. 3. Fig. 3a shows luminescence spectra taken from different points in the microscope image of Fig. 2b. They are quite broad (and seem multiband) covering all visible spectral range with principal maximum at  $\sim 550$  nm. This indicates a heterogeneous nature of the luminescence band, which supports our hypothesis about the broad size distribution of deposited silver particles, issued of the absorption measurements. Previously, broad spectra (however, with distinct multiband character) were observed and assigned to a particular cluster-size distribution [30].

A particular feature of our recorded spectra is their almost similar lineshape measured in points with much different brightness. The measurements evidence that the photocatalytic coverage of the nanoparticle  $\text{TiO}_2$  substrate by silver clusters is highly uniform at the scale below  $10^2$  nm (size of  $\text{TiO}_2$  agglomerate unit). The sample morphology accounts for more uniform hot spots distribution



**Fig. 3.** Luminescence spectra of  $\text{Ag}_N/\text{TiO}_2$  sample from different hot spots (a) and at different power of laser excitation (b): (1)  $P_L = 1$  mW; (2) 4 mW; (3) 7.6 mW; (4) 11.6 mW; (5) 15.4 mW; (6) 19.7 mW. Inset: the dependence of luminescence vs. excitation power in the log–log coordinates. The slope equals  $1.95 \pm 0.03$ .

combined with highly uniform emitters composition, compared to that in fractal-like aggregates formed by precipitation of silver colloids. We remark that in our separate experiments two samples were prepared by precipitation from silver colloid (direct salt photolysis) on  $\text{TiO}_2$  and on glass plate: as-prepared samples exhibited multicolor luminescence under fs near-IR laser excitation in agreement with literature data [27].

Silver clusters and nanoparticles are known to form Shottky junction on contact with  $\text{TiO}_2$  nanoparticles. It was recently shown that the photon absorption in the plasmon band is accompanied by the excited electron injection into the semiconductor conduction band [31]. This is quite important for creation of luminescence centres, while  $\text{Ag}^+$  ions are suggested to stabilise smallest oligomeric silver clusters  $\text{Ag}_N$  ( $N \leq 10$ ) [32,33]. Accordingly, silver clusters are formed that is responsible for a broad multiband visible luminescence. Intensity maximums around 550, 600, 650 and 700 nm were earlier observed; individual particles were found to display different colours and strong intensity fluctuations (blinking) [34]. Charge state plays an important role in  $\text{Ag}_N$  optical properties. In particular, radiolysis experiments have revealed the dominant role of  $\text{Ag}_{4+x}^{x+}$  and  $\text{Ag}_7^{3+}$  clusters in luminescence, respectively, at 550 and 700 nm. Their long-wave absorption bands were correspondingly observed at 470 and 580 nm [34]. Our measurements confirm multiband character of silver luminescence, which is related to clusters of different size and charge state. However, we cannot evidence the charged oligomeric clusters from the absorption measurements. Apparently, large silver nanoparticles dominate absorption of our samples. They contribute to the EF enhancement that stimulates emission of small silver clusters.

Fig. 3b presents luminescence spectra of  $\text{Ag}_N/\text{TiO}_2$  sample with fs near-IR laser excitation at different excitation power. These spec-

tra were collected from a wide-field area of  $25 \times 25 \mu\text{m}^2$ , integrating intensity over hundreds hot spots. This approach is appropriate because of the above discussed sample homogeneity. These spectra exhibit significant blue shift by  $\sim 50$  nm with an increase of the laser power, which may be related to the excited state population provided the relaxation within this state is faster than quenching.

The inset in Fig. 3b demonstrates nonlinear character of the luminescence excitation. Accordingly, the luminescence intensity grows up as a square of femtosecond near-IR laser power. The linear fit of the experimental data evidences the slope of 2 in the logarithmic frame. Two 800 nm photons cannot afford the interband transition (VB  $\rightarrow$  CB) of oxo-alkoxy  $\text{TiO}_2$  nanoparticles [17], which in turn possess no resonant intraband impurity or defect states capable masking the transition order due to saturation effects. We conclude that this luminescence results from the direct laser excitation of silver clusters. The observed luminescence is consistent with two-photon surface-plasmon-mediated luminescence of oligomeric silver clusters, enhanced by presence of larger silver nanoparticles and activated through interfacial electron transfer to  $\text{TiO}_2$  nanoparticles.

We remark that the luminescence of pristine  $\text{TiO}_2$  is extremely weak and is positioned in the same spectral range as that of silver clusters: 400–800 nm with the maximum at 550–600 nm [35]. Its enhancement may contribute to the observed spectra. The role of the energy and electron transfer between silver and  $\text{TiO}_2$  clusters is an important issue of future studies.

#### 4. Conclusion

The deposition of silver clusters on non-crystalline  $\text{TiO}_2$  sol nanoparticles was achieved by heterogeneous photocatalytic reduction of silver nitrate solution under UV-irradiation. This particular  $\text{TiO}_2$  system possesses structural hierarchy, which results in the characteristic distance between surface-positioned silver clusters of  $\sim 10$ – $10^2$  nm that is favourable for EF enhancement.

Luminescence properties of the prepared  $\text{Ag}_N/\text{TiO}_2$  samples were studied with two-photon excitation by 100 fs laser pulses at 800 nm. The luminescence is assigned to oligomeric clusters activated by interfacial electron transfer to  $\text{TiO}_2$  nanoparticles and enhanced by presence of larger silver nanoparticles. It exhibits a point-like character: the bright points of size  $\leq 0.1 \mu\text{m}$  on microscopic images suggest a presence of hot spots inherent to plasmon localization effect.

The measurements evidence that size distribution of silver clusters over the sample area is highly uniform on the scale equal or smaller than  $10^2$  nm. This results in spatially uniform and reproducible EF-enhanced luminescence spectra.

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