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Three-photon-induced luminescence of gold nanoparticles embedded in and located on the surface of glassy nanolayers

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Abstract

We report on the multiphoton-induced luminescence of gold nanoparticles embedded in thin glassy silicate–titanate films. The glassy layers doped with gold(III) chloride are synthesized by a sol–gel coating process. Gold nanoparticles are generated by subsequent annealing of the thin films at 300 °C. Intensive near-infrared femtosecond laser irradiation also initiates the formation of gold particles, providing the possibility of spatially resolved photoactivation of the film. The reduction of gold ions to gold nanoparticles is monitored by Au L₃-edge x-ray absorption near edge spectroscopy (XANES), UV–vis absorption spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The particle sizes and shapes can be tuned by changing the metal concentration in the matrix. We demonstrate that the particles exhibit an efficient, long time stable, white luminescence during near-infrared Ti:sapphire femtosecond laser excitation. The laser power-emission intensity law indicates that the luminescence is induced by the absorption of three laser photons. Cross-sectional TEM images show that gold nanoparticles are both embedded in the glassy matrix and located on the film surface. Hence, the particles should be accessible for viable applications, for example as sensor materials, and could therefore become a powerful alternative to organic and semiconducting fluorophores in biological imaging.

1. Introduction

Although noble metals have been investigated for many years, the optical properties of noble metal thin films, nanoparticles or small molecular clusters are more than ever at the focus of research [1–3]. While the optical properties of gold-containing stained glasses and colloidal metal solutions have already been described by the fundamental work of Faraday in 1857 [4] and especially Mie in 1908 [5] by solving Maxwell’s equations for the interaction of electromagnetic light waves with spherical metal particles, a physical interpretation of the extraordinarily large absorption and scattering cross sections was given much later by introducing the phenomenon of the surface plasmon polariton [6, 7]. As in the Drude model for a free electron gas, a uniform external electric field can induce a dipole in a metal particle, causing a uniform displacement of the electron cloud to cancel the internal electric fields. In this approximation an oscillating external field can induce collective electron oscillations at a metal specific surface plasmon polariton resonance (or surface plasmon resonance, SPR) frequency. This phenomenon is similar to the excitation of surface plasmons when fast electrons are scattered inelastically by thin solid metal films [8].
The quantum yield was estimated to just $10^{-15}$, hence metals have been treated as (nearly) non-luminescent for a long time. However, 30 years later single-photon-induced visible PL of gold nanoparticles no larger than 5 nm was discovered. Furthermore, it could be ascertained theoretically and experimentally that the quantum yield of rod-shaped particles is enhanced compared to spherical ones. The enhancement factor can be as high as $10^6$ in relation to the PL quantum yield of bulk surfaces [11, 12]. Recently it has been shown that the PL of miscellaneous nanoscopic gold objects can be efficiently excited by multiphoton absorption due to electric field enhancement effects. For example, irradiation of gold films, nanoparticles and sharp gold tips with the fundamental of a Ti:sapphire femtosecond laser at 780 nm induces a white and near-infrared (NIR) luminescence caused by two-photon absorption [13, 14]. Farrer et al [15] even investigated a white PL, which was caused by the absorption of three laser photons with a wavelength of 790 nm. This strong light emission during the excitation of gold particles at NIR wavelengths could become extremely useful for biological and medical applications like in vivo imaging, because of the transparency of and reduced cell damage to human and animal tissues in this spectral range.

But new applications based on luminescence cannot be accomplished unless the investigated light emitting materials remain chemically and mechanically stable under long time irradiation and the particles can be reproducibly synthesized. Inorganic glasses are very suitable matrices for the generation of noble metal nanoparticles in narrow size distributions [16]. The sol–gel coating process is a very capable technique for synthesizing several functional compounds like gold nanoparticles embedded and stabilized in thin glassy layers [17, 18]. The matrix and its optical properties like the index of refraction can be easily tuned by choosing different precursor alkoxides. Gold nanoparticles can be generated by annealing or irradiating the gold-doped layers with UV light [19, 20].

As reported above, many experiments on the PL of gold films and relatively large nanoscale gold objects have been made. However, to the best of our knowledge only a few systematic reports on the multiphoton-induced luminescence of smaller nanoparticles have been published [15]. But these studies are necessary to clarify the newly found unusual three-photon-induced PL of gold nanoparticles and, last not least, because of the possible practical relevance of these particles as luminescence markers. In this report we describe the generation of gold nanoparticles in thin silicate–titanate layers by annealing or NIR laser irradiation. Particle size, shape and consequently the SPR frequency can be tuned by changing the metal concentration in the matrix. These clusters exhibit an efficient white multiphoton-induced luminescence during NIR Ti:sapphire femtosecond laser excitation. The gold nanoparticles are both embedded in the glassy matrix and on the surface and thus should be accessible for manifold applications like optical memory, surface-enhanced Raman scattering (SERS) [21], catalysis and sensor technologies.

2. Experimental section

All chemicals were used as-received without further purification. Gold-doped glassy layers were synthesized by the sol-gel coating technique. Firstly, appropriate amounts of gold(III) chloride hydrate (puriss. p.a., Fluka) were dissolved in 6 ml absolute ethanol with 200 µl 2 M hydrochloric acid as catalyst for hydrolysis. 1.57 ml tetraethyl orthosilicate (99.999%, Sigma-Aldrich) and 0.63 ml titanium(IV) ethoxide (for synthesis, Merck) were added. Samples with 0, 3, 5, 10 and 20 mol% gold (related to the total amount of Si and Ti) were prepared. Soda-lime silicate glass substrates with sizes of $10 \times 10$ mm$^2$ and thicknesses of 1 mm were coated with the sol–gel via spin-coating at 3000 rpm for 40 s. Subsequent annealing for 10 min at $300^\circ$C was accomplished in a tube furnace (Heraeus Ro 4/25 with control unit Heraeus Thermicon P) immediately after the coating process.

UV-vis absorption spectra were acquired with a fiber optic spectrometer HR2000 (Ocean Optics) and a deuterium tungsten halogen light source (Stellar Net).

Au L$_2$-edge x-ray absorption near edge spectroscopy (XANES) was carried out at the BAM line of the Berlin electron storage ring facility BESSY. Spectra were recorded in fluorescence mode (detection at the Au L$_\alpha$ line at 9707 eV) between 11 900 and 11 990 eV with an increment of 1 eV. Peak integration was determined with the program QXAS 3.5. Background correction was done by subtracting the absorption value at 11 900 eV and normalization of the value at 11 990 eV to unity.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) measurements were made at the Fritz-Haber-Institut of Max-Planck-Gesellschaft in Berlin with a Philips CM 200 LaB$_6$ microscope operating at an acceleration voltage of 200 kV and a Hitachi S-4800 field emission scanning electron microscope, respectively.

The experimental setup for performing multiphoton laser scanning microscopy consisted of a commercial Leica TX confocal microscope which was adapted to receive light from a home-built Ti:sapphire oscillator with a repetition rate of 84 MHz. Additional dispersion compensation with a prism compressor and a special near infrared (NIR) objective (XLUMPlan FL, $20 \times$, NA = 0.95 (water)) enabled the generation of 60 fs pulses in the focal plane of the microscope at a center wavelength of 795 nm. The emitted photons were collected with the same objective. A dichroic mirror in combination with longpass filters was used to separate excitation from luminescence light. Two-dimensional PL images of the samples were acquired by using a biaxial pivoted scanning mirror. The luminescence photons were detected by a photomultiplier to yield 8 bit gray-scale images.

The excitation source for the spectrally resolved photoluminescence measurements was a Clark CPA 2001 Ti:sapphire femtosecond laser that produces 130 fs pulses at a center wavelength of 775 nm with a repetition rate of 1 kHz. Samples were irradiated on the coated side at an angle of incidence of 40$^\circ$ with a pulse energy of 100 µJ. The beam was slightly focused in order to reach a maximum intensity of approximately 2.5 GW cm$^{-2}$. The emitted luminescence was collected opposite to excitation and perpendicular to the substrate and further imaged onto the entrance slit (slit size 500 µm) of a grating monochromator. The excitation light was filtered using two Linos Calflex X bandpass (400–700 nm) filters or a shortpass Schott BG 39 filter (thickness 2 mm, transmission $\leq 0.01$ for $\lambda \geq 700$ nm). The luminescence was detected by a liquid nitrogen (LN$_2$)-cooled CCD camera. The detector integration time
was set to 5 s. For detailed luminescence spectra the PL was measured at two different monochromator positions to cover the whole visible spectral range and with an entrance slit size of 100 μm to obtain the highest possible spectral resolution. The setup was calibrated using a mercury calibration lamp at the different monochromator positions. The acquired spectra were corrected for background counts, filter transmission and spectral sensitivity of the CCD camera. The laser intensity for the laser power dependence experiment was attenuated with gray filters and measured with the fiber optic spectrometer SD2000 (Ocean Optics) in scope mode by integrating the obtained laser spectra. All spectra were measured at room temperature.

3. Results and discussion

3.1. Characterization of the gold-containing thin films

The gold-containing thin films were characterized by UV–vis absorption spectroscopy (figure 1). After the sol–gel spin-coating process the films were colored slightly yellow. Hence, an absorption at wavelengths ≤400 nm can be identified in the spectrum caused by tetrachloroaurate(III) anions. After annealing for 10 min at 300 °C the formation of gold nanoparticles is evidenced by the characteristic gold surface plasmon absorption and the appropriate ruby-red to violet color. With increasing gold concentration from 3 to 20 mol% the maximum of the surface plasmon absorption is shifted from 540 to 570 nm and the FWHM is increased. The absorption at wavelengths <500 nm is due to gold interband electron transitions between the 5d and the 6sp conduction band. In contrast, undoped films are transparent in the visible spectral range independent of the annealing procedure. At wavelengths <350 nm the soda-lime silicate glass substrate starts to absorb.

The state of oxidation before and after annealing was determined by XANES at the Au L3-edge (figure 2). In our studies gold(I) cyanide, tetrachloroauric(III) acid and gold bulk as reference materials for the different viable oxidation states 0, +I, and +III of gold were measured for comparison. Cationic gold standards show distinct peak maxima (so-called white lines) at 11 923 eV (Au+1) and 11 927 eV (Au+) due to transitions of 2p electrons into vacant 5d states, and can be clearly distinguished from Au0 samples, whose spectra do not contain any white line transitions. Comparison of the glass sample and reference spectra ascertains that gold is in the oxidation state +III before the annealing process. The spectra and especially the white lines of the tetrachloroauric(III) acid and the unannealed sample match almost exactly, which also indicates that gold is still embedded as tetrachloroauric(III) ion in the glassy matrix. After annealing at 300 °C the white line has vanished and the absorption edge is shifted from 11 920 to 11 921 eV. This can be explained by a complete reduction of gold(III) to atomic gold, also shown by the good overlap between the glass sample and gold bulk reference spectra. The reduction process is in accordance with the observed SPR peak of gold nanoparticles in the UV–vis spectra described above.

The gold particle diameters and the film thicknesses were determined with TEM. Cross-sectional TEM images of the sample containing 10 mol% Au after annealing show a homogeneous distribution of gold nanoparticles within the silicate–titanate layer (figures 3(a) and (b)). The clusters are spherical and have a mean diameter of 10±4 nm. The thickness of the doped film is 350 nm. It is remarkable that particles with nearly the same size and shape as the embedded ones are also located on the surface of the film. The gold clusters on the surface were investigated by SEM (figures 3(c) and (d)). The SEM images show a homogeneous distribution of spherical particles, which is in accordance with the TEM investigations.

The same measurements were done for a sample containing 20 mol% gold after annealing for 10 min at 300 °C. As a result, we obtained a film thickness of 350 nm, too. However, the cross-sectional TEM images indicate a large size distribution of gold nanoparticles of various shapes (figures 4(a) and (b)). The diameters of the particles vary typically between 5 and 100 nm. Triangles, hexagons, rods and other objects can be found in addition to spherical clusters. The nanoparticles are both embedded within the glassy matrix and situated on the surface of the layer. The SEM investigations of the surface affirm the trend of the TEM measurements. Similar shapes and sizes as in the TEM images can be identified in the images (figures 4(c) and (d)).
We shall now try to explain the different particle size distributions of the samples containing different amounts of gold. Under ideal conditions the cluster growth process in glasses can be separated into three stages: the formation of critical nuclei, the diffusion of atoms to the nuclei with the subsequent diffusion-limited growth of clusters and the ripening process, where larger particles grow at the expense of smaller ones to minimize the surface tension [22]. During the annealing of the glassy layers nucleation and growth of smaller clusters occur synchronously. But in the case of low concentrations the particle distances may be large enough to avoid the ripening process during the short annealing period of 10 min. Additionally, the hardening of the silicate matrix decreases the mobility of the gold atoms, leading to narrow gold particle size distributions. Obviously, for the high concentration of 20 mol% gold, the ripening stage cannot be ignored. Consequently, the simultaneous nucleation, growth and ripening processes induce large size and shape distributions.

With this knowledge it is also possible to interpret the UV–vis spectra of the thin films containing different amounts of gold mentioned above (figure 1). The observed red shift of the SPR absorption from 540 nm for 3 mol% gold to 570 nm for 20 mol% gold-containing samples and the increasing FWHM of the SPR peak can be explained by the increasing size of the particles due to retardation effects, SPR damping phenomena and excitation of higher multipoles [7, 23]. Another reason is certainly the increasing deviation from the spherical shape, i.e. a red shift of the SPR is achieved by an increasing aspect ratio of noble metal ellipsoids (and consequently an increasing deviation from the spherical shape) caused by electromagnetic field enhancements due to the higher polarizability of nonspherical particles [12, 24, 25].

3.2. Multiphoton-induced luminescence

To study the photoluminescence of the gold nanoparticles, the glass samples were first investigated by confocal laser scanning microscopy. For this purpose, the glasses were excited with femtosecond pulses of a Ti:sapphire laser at a center wavelength of 795 nm. As a result, only annealed layers containing gold nanoparticles show a bright luminescence during excitation. Undoped or unannealed samples do not luminesce at all. Obviously, the light emission is caused by gold nanoparticles, because the annealing step is necessary for both the formation of particles and the PL. Interestingly, excitation with a laser power in the range of 1 GW cm$^{-2}$ causes an effective bleaching of the irradiated area. In this way, micrometer-sized squares have been written into the sample (figure 5(a)), which could be read out at a laser power of approximately 0.2 GW cm$^{-2}$ without further bleaching. However, the laser can also be used to write luminescent structures into unannealed (and originally non-luminescent) gold-containing films (figure 5(b)). This activation was done with a power of 1 TW cm$^{-2}$ within seconds. These spots can also be identified by their violet color due to the surface plasmon absorption of gold nanoparticles that have been formed obviously during the irradiation process. It is well known that gold nanoparticles can be generated in silicate films by UV irradiation [19]. In the case of NIR laser irradiation a multiphoton process is most likely, and this has to be proved in advanced experiments. At read-out powers of 0.2 GW cm$^{-2}$ no further activation or bleaching occurs. These observations are promising for the use of the glassy films as optical data storage materials.

Furthermore, PL spectra were recorded with a grating monochromator and a LN$_2$-cooled CCD camera. For this purpose, the thin glassy films were excited with the fundamental of a Ti:sapphire femtosecond laser at 775 nm with a maximum pulse energy of 100 μJ. Scattered excitation light was blocked by a bandpass filter. The investigation of samples with different amounts of gold indicates that only annealed films containing gold show a white luminescence (figure 6), which can be seen with the naked eye. The run of
Figure 5. False-color laser scanning microscopy images of silicate–titanate films containing 20 mol% gold. Image sizes are 500 × 500 μm². (a) Sample annealed for 10 min at 300 °C. Bleached (dark-brown) squares were written with a laser power of 1 GW cm⁻² (120 000 laser shots/pixel). Square sizes are 15 × 15, 40 × 40, and 140 × 140 μm². (b) Unannealed sample. The (bright) luminescent lower part was written with a laser power of 1 TW cm⁻² (120 000 laser shots/pixel).

Figure 6. Photoluminescence spectra of silicate–titanate films annealed for 10 min at 300 °C and containing different amounts of gold. Monochromator entrance slit size: 500 μm.

Luminescence spectra between 400 and 700 nm were obtained by combining data sets measured at two different grating monochromator positions (figure 7). Two slight maxima at 480 and 600 nm can be identified. For the glassy film containing 10 mol% gold the PL spectrum was compared with its UV–vis spectrum. Additionally, an absorption spectrum using the quasi-static approximation of Mie theory [5, 7, 16] was calculated for gold particles with diameters of 10 nm—the mean value found by TEM and SEM measurements—in a silicate–titanate (2:1) matrix with an refractive index of 1.60. As a result, an excellent agreement between measured and calculated spectra was obtained, which confirms the monodispersity and thus the accordance between the expected optical properties and the size of the gold particles embedded in the glass. The two PL maxima could be interpreted in terms of discrete transitions between electronic states or of a surface plasmon emission. However, the discrepancy between the PL maxima and the SPR, but the coincidence between the SPR and the PL minimum at approximately 550 nm, suggests that the lack of luminescence intensity at this wavelength is due to an absorption of luminescence photons by surface plasmons.

For the interpretation of the PL spectra it is important to investigate the dependence of the luminescence intensity from the laser power. The results of the PL measurements at different laser intensities are depicted in figure 8(a). Logarithmic plots of the integrated emission intensity versus laser power for the 20 mol% containing sample gives a slope of 2.9. The appropriate value for the film with 10 mol% gold is 2.4. To make sure that scattered laser light does not distort the measurements, we also used a setup with a shortpass filter, that blocks even more effectively the light at wavelengths ≥ 700 nm than the bandpass filter used before. In this configuration a slope of 3.1 was obtained for the 20 mol% gold-containing layer.

These findings indicate that excitation of the samples with the highest amount of gold is a three-photon process. The slope of 2.4 for the 10 mol% gold-containing films could be interpreted in terms of a mixture of a two- and three-photon excitation. But one has to take into account that the measured dependence is not perfectly linear as in the case of the higher-doped samples and that the lower emission intensities make this value much more uncertain. Nevertheless, a slope of 2.4 is also a supporting fact for a minimum involvement of a three-photon process. The PL counts at wavelengths below 387.5 nm (which corresponds to the second harmonic of laser fundamental), found for all annealed samples that contain gold particles, are another strong hint for three-photon absorption.
For gold particles with a diameter of 100 nm [13], rough gold films [13, 26], sharp gold tips [13] and gold bowtie nanoantennas (lengths of about 75 nm) [27] a two-photon-induced PL is implied. In contrast, Farrer et al. reported recently on a three-photon absorption induced luminescence of 15 nm silica-coated gold particles [15]. The following reasons can be taken into consideration in accounting for the different observations: (1) The nanoparticles investigated by Farrer et al. have a similar size and shape to the particles studied in our experiment. Larger particles or gold structures have a higher density of states and this could cause different optical properties. Additionally, large gold structures have a red-shifted and broadened SPR, which should have an influence on the PL efficiency of two- and three-photon processes, respectively. (2) The particles are embedded in a similar (silicate) matrix, too. The dielectric environment can play a significant role in the efficiency of the multiphoton-induced luminescence, i.e. PL can be quenched or enhanced due to energy transfer processes. (3) The excitation and PL intensity of the larger gold objects reported in the literature was lower [13]. Consequently, the excitation may have been performed at laser intensities favoring two-photon processes.

Several experimental results in the literature support the observation of three-photon-induced PL. A three-photon absorption at 775 nm corresponds to a single-photon absorption at 258 nm. Indeed, Wilcoxon et al. [10] detected a PL of 5 nm gold particles during excitation at 230 nm. El-Sayed et al. [24] reported on the luminescence of 25 nm gold clusters, which could be excited in a single-photon process at 267 and 410 nm. Interestingly, the quantum yield was the same for both excitations. Consequently, a two- and three-photon process should be possible for gold nanoparticles during excitation at 775 nm. The probability should be dependent only on laser power.

It is often argued that the emission of light follows the excitation of electron transitions from the 5d to the 6sp bands [11, 26, 28]. This has already been postulated for bulk metals by Mooradian in his work on the PL of gold and copper surfaces [9]. A schematic representation of possible excitation and emission paths close to the L symmetry point of the band structure of gold is depicted in figure 9.

However, the quantum yield of the emission of gold films was estimated to only $10^{-10}$. Therefore, the giant enhancement observed for nanoparticles has to be explained. In principle, luminescence quantum yields can be enhanced by two different mechanisms: (1) a deceleration of radiationless relaxation processes and (2) an acceleration of radiative transitions. The quenching of the PL in metals is mainly caused by electron–electron or electron–phonon scattering. A deceleration can be observed for very small molecular metal clusters due to their lower electronic density of states [29]. However, in nanoparticles with diameters larger than 2 nm these processes are as fast as in the bulk or even accelerated [30, 31]. The second idea of an accelerated
Indeed was observed in a single-photon excitation study [36]. Should directly correlate with the SPR absorption, which would only be due to surface plasmon emission, the PL spectra (continuum) in the case of multiphoton excitation. If the PL observe a white PL covering the whole visible spectral range of the SPR spectrum and the PL was achieved. But we indeed, for a single-photon process a nearly perfect overlap thirdly, decay radiatively and thus give rise to the observed PL. Momentum-conserving excitation of surface plasmons which, d-band holes relax to d-band states under the energy- and due to the excitation of electrons into the sp band. Secondly, this indicates that the PL is not due to surface plasmons, which can only be excited in nanometer-sized objects like nanoparticles, rough films, etc [11, 26]. The local optical fields of nanoparticles, and especially aggregates of them, are strongly localized in regions even smaller than the excitation wavelength, often called ‘hot spots’ [32]. The electromagnetic enhancement mechanism is the most often discussed explanation for the surface-enhanced Raman scattering effect. If the incident and Stokes-shifted frequencies are in the range of the surface plasmon resonance frequency, the Raman scattering signal of a molecule located at a hot spot is enhanced by a factor $E$ given by the equation $E = |E(\omega)|^2|E(\omega')|^2$, with $E(\omega)$ and $E(\omega')$ being the local electric field enhancement factors at the incident and Stokes-shifted frequencies, respectively [33]. This mechanism was also proposed for the observed fluorescence enhancement of molecules (or adjacent noble metal particles) near plasmonic gold or silver objects [34, 35]. While in SERS experiments molecules are normally adsorbed at the surface of the metal particles, the enhanced fluorescence is only observed for molecule–nanoparticle distances of several nanometers. That is why Dulkeith et al [28] cast into doubt an enhancement of the gold nanoparticle fluorescence of 4–6 orders of magnitude by this process alone, because a local field enhancement in this case would be only of the order of 10. They suggest the following mechanism instead: firstly, d-band holes are created due to the excitation of electrons into the sp band. Secondly, d-band holes relax to d-band states under the energy- and momentum-conserving excitation of surface plasmons which, thirdly, decay radiatively and thus give rise to the observed PL. Indeed, for a single-photon process a nearly perfect overlap of the SPR spectrum and the PL was achieved. But we observe a white PL covering the whole visible spectral range (continuum) in the case of multiphoton excitation. If the PL would only be due to surface plasmon emission, the PL spectra should directly correlate with the SPR absorption, which indeed was observed in a single-photon excitation study [36].

Radiative process is therefore more likely to explain the PL enhancement. Some research groups proposed that the light emission is enhanced by the local field associated with the surface plasmons, which can only be excited in nanometer-sized objects like nanoparticles, rough films, etc [11, 26]. The particles investigated in our work have diameters between 5 and 100 nm and the SPR peaks in the UV–vis absorption spectra are shifted from 540 to 570 nm with increasing gold concentration (and increasing particle diameter). However, no obvious tendency to be correlated with the SPR can be identified in the PL spectra. Consequently, these findings suggest a contribution of direct radiative transitions between excited sp-band electrons and d-band holes rather than a plasmon emission to the PL. Accordingly, the PL continuum could mirror the joint density of states between these two bands.

A logarithmic plot of the integrated PL intensity versus gold concentration and the linear regression gives a slope of approximately 3 (figure 10(a)). The value for the lowest concentration of 3 mol% does not fit the linear regression, but the PL is very weak and the error due to a low signal-to-noise ratio is large. Therefore this data point is ignored. For single-photon processes the emission intensity was found to be proportional to the cube of the particle radii and consequently directly proportional to the particle volume [28]. In the case of a three-photon excitation the PL should be dependent on the cube of volume and thus on the cube of concentration. Indeed, this is observed in our experiment. Obviously, the multiphoton-excited PL also depends on the volume of the particles and is independent of the shape or distance between particles. Furthermore, this indicates that the PL is not due to surface states. In this case the PL would depend on the surface/volume ratio instead.

As mentioned in the introductory remarks, photostability is indisputable for the long term usage of the glassy thin films for sensor or optical memory applications. A strong bleaching and blinking behavior is often a disadvantage of classical luminescence markers like organic molecules and inorganic semiconductors. Long time luminescence measurements showed that our samples bleach only at the very beginning of the laser excitation (applied for microstructuring in figure 5(a)) and that the PL decreases by less than half (figure 10(b)). After approximately 60 s the emission intensity remains stable for up to hours. Even after storage at room temperature for more than a year no deterioration has been observed.

![Figure 10](image-url)

**Figure 10.** (a) Logarithmic plots of the integrated emission intensity versus gold concentration for annealed silicate–titanate films containing 3, 5, 10 and 20 mol% gold and linear regression of the data points of 5, 10 and 20 mol% gold films. (b) Typical bleaching curve of a silicate–titanate film containing 10 mol% gold after 10 min annealing at 300 °C during Ti:sapphire laser excitation at a power of 1 GW cm$^{-2}$ (number of laser shots = time[s] × 10$^6$ s$^{-1}$).
4. Conclusions

We have shown that gold nanoparticles can be embedded and stabilized in 350 nm thin silicate–titanate films prepared by a sol–gel spin-coating technique and subsequent annealing at 300°C or, alternatively, NIR femtosecond laser irradiation. In the latter case structuring of the film with a scanning laser microscope also becomes possible. The size of the particles ranges between 5 and 100 nm and can be tuned by choosing the gold concentration. While a lower concentration of up to 10 mol% favours smaller and spherical clusters with a narrow size distribution, larger concentrations induce the growth of nonspherical structures. NIR Ti:sapphire femtosecond laser excitation of the thin films induces a strong white PL covering the whole visible spectral range. The analysis of the dependence of the PL intensity on laser power indicates a three-photon absorption induced process. The analysis of the PL intensity on laser power indicates a three-photon absorption induced process. The samples are photostable, stable against contact with solvents like water, ethanol and acetone, and can be stored at room temperature without deteriorations of the optical properties. Electron microscopy investigations have shown that the particles are not only embedded within the matrix but are also located on the surface of the film. Advanced experiments indicated SERS activity of the gold-containing films towards the nucleobase adenine, which proved the accessibility of the surface gold nanoparticles to bio-organic molecules. Hence, the thin films should have potential for application in sensors based on SERS spectroscopy and/or the multiphoton-excited PL and thus could represent a powerful alternative to organic luminescence markers.

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