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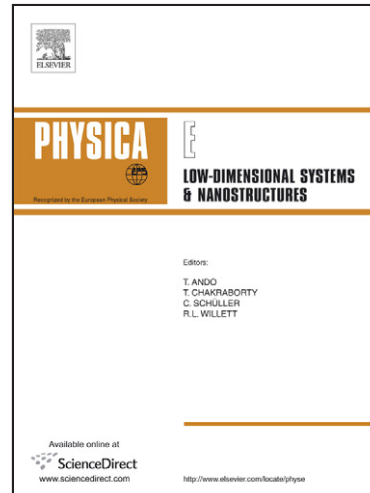
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TWO-PHOTON EXCITATION OF LUMINESCENCE IN PYROLYTIC SILICON NANOCRYSTALS

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ABSTRACT

Two-photon excited luminescence after femtosecond NIR excitation was observed in chemically oxidized silicon nanocrystals (Si-nc) produced by laser-assisted pyrolysis of silane. The luminescence time decay and emission spectrum resulted in good agreement with those after blue excitation. The underlying two-photon absorption coefficient was also measured by the open-aperture z-scan technique, obtaining a value of 12.5 cm/GW, which is intermediate between the values reported in the literature for bulk silicon and for very small Si-nc.

INTRODUCTION

Silicon nanocrystals (Si-nc) are being extensively investigated because of their widespread potential applications ranging from photonics[1] to photovoltaics[2] and to biological imaging[3]. Important assets of Si-nc based materials are the compatibility and possible knowledge exchange with current microelectronics technology, their low toxicity, and the low-cost availability of silicon.

Photoluminescence (PL) emission from Si-nc is a key property for several applications if not all, and as such it has been the subject of numerous studies. Although the mechanism of the emission has long been controversial, there is now a general agreement on a model based on the emission from trap-states at the interface of oxidized particles[4], occurring in the red or near infrared region, and on the intrinsic emission from band to band recombination which can be more blue shifted in the green-blue region.

Oxide-coated particles are well suited for biological imaging applications since they are stable, efficiently emitting, and moreover their surface can be easily functionalized for bio-conjugation. Because of their low toxicity and stability, one of the most appealing possibilities is their employment to replace currently investigated[5] II-VI quantum dots or organic fluorophores for in-vivo imaging. For this application, two-photon excitation of luminescence (TPE) using near-infrared (NIR) lasers presents a number of advantages, as increased spatial resolution, in depth excitation inside biological tissues and minimization of background luminescence from biological surroundings. A necessary prerequisite for two-photon excitation of luminescence is nonlinear or two-photon absorption (TPA) in the NIR, where linear absorption is negligible. The absence of linear absorption in the infrared, and the necessary occurrence of TPA mark the difference of TPE with respect to other anti-Stokes luminescence effects caused by Auger interaction between excitons [6], or by excited state absorption. TPA was indeed observed at 813 nm in Si-nc composites prepared by plasma-enhanced CVD [7]. Two-photon absorption and PL emission were observed in porous silicon[8], which falls in the category of Si-based nanomaterials but has special fabrication procedure, morphology and surface termination. Because of the well-known dependence of the properties of Si-nc on the preparation methods, surface termination and dimension, it is useful to investigate TPE and TPA on a different class of material, namely pyrolytic Si-nc, which are promising candidates for in-vivo bio-imaging.

Here we first show the occurrence of two-photon absorption in a Si-nc suspension by measuring the TPA coefficient under femtosecond NIR excitation using the well-known[9] open-aperture z-scan

technique . Then we report on luminescence emission centred at 750 nm from dry oxidized Si-nc after NIR femtosecond two-photon excitation, and we compare this emission with that excited by one-photon absorption. Silicon nanoparticles used in this experiment were prepared by laser-assisted pyrolysis of silane, which is a process which permits the preparation of grams of ultra-pure powders[10], that can be easily processed for preparation of functional materials.

EXPERIMENTAL

Open-aperture z-scan measurements were performed on a pristine nanopowder with 6 nm crystalline core diameter as obtained by X-ray diffraction analysis [11]. The Si-nc powder was dispersed in methanol with the help of a high power ultrasonic tip, at concentration equal to 2 g/l, corresponding to a silicon volume fraction equal to about 0.86×10^{-3} . The suspension was placed inside a 1 mm thick quartz cuvette. The sample was excited using a tunable femtosecond Ti:Sapphire laser equipped with a cavity dumper for control of output pulse repetition rate, and focused with a 5 cm focal length lens. For z-scan measurements the laser pulse repetition rate was reduced to 270 Hz to minimize sample heating and thermal lens effects. The laser was tuned to 900 nm with a maximum pulse energy in the range 40-60 nJ and with a pulsewidth equal to 120 fs as measured using an on-line autocorrelator. In our experiment the pulse energy could be varied by changing the RF power applied to the acousto-optic modulator in the laser cavity dumper. Calibration of pulse fluence was obtained using a CS₂ reference sample, for which we used a nonlinear refractive index equal to 3×10^{-6} cm²/GW [12].

Luminescence emission from pyrolytic Si-nc can be obtained by oxidation due to aging or post-processing [13,14]. In the present case the powder used for luminescence experiments was chemically oxidized using a wet process, eventually producing a dry powder showing stable and efficient luminescence emission band centered around 750 nm, when excited in the blue/green region[14]. For the wet chemical oxidation, pristine silicon nanoparticles were treated at T=60 °C in a solution of H₂O₂ and NH₄OH at a 1:1 ratio in methanol which was also used as dispersion

medium. The oxidized powder was separated by centrifugation and decantation and finally dried. As detailed elsewhere[14], this process improves the stoichiometry of the surface oxide without substantial etching of the inner silicon crystalline core, increasing the luminescence emission of more than one order of magnitude. For luminescence measurements the silicon nanoparticle sample was slightly pressed by hand on a microscope glass to form a small pellet of few hundred micron thickness, and was kept in place by a cover glass. The crystalline core size distribution of the sample used in this experiment was peaked at 4.4 nm, with a FWHM equal to about 4 nm, as obtained by analysis of the X-ray diffraction pattern[11].

The TPL was excited using the femtosecond Ti:sapphire tuned at 900 nm with a pulse repetition rate set to 1-5 kHz, corresponding to a pulse spacing of 200-1000 μ s, much longer than the luminescence decay time, in order to avoid multiple excitation of the Si-nc. For efficient TPL generation, the laser beam was focussed onto the sample using a 5 cm focal length lens,. The sample was tilted at about 45 degrees with respect to the incident beam direction to facilitate collection of luminescence by a 20X long-working-distance microscope objective (N.A=0.4). The light collected by the objective was delivered to two different detection systems for measurements of the emission time decay and of the emission spectrum respectively. The time decay was measured using a photomultiplier tube equipped with a gated socket for efficient suppression of the initial laser pulse spike. A bandpass filter centred at 750 nm was placed in front of the photomultiplier. The emission waveform was captured and saved by a digital oscilloscope, and then transferred to a PC for analysis.

To measure the emission spectrum, the light collected by the objective was fiber-launched and delivered to a 550 mm focal length spectrograph coupled to a liquid nitrogen cooled CCD. An 850 nm cut off short pass filter was placed in front of the collection optics to increase rejection of the 900 nm pump laser beam. Measured spectra were not corrected for the detection system response.

For measurement of the one-photon excited luminescence, the Ti:sapphire laser was equipped with a second-harmonic generation unit, which produced a maximum pulse energy equal to 11 nJ at 450

nm. Scattering of exciting radiation in the pellet sample is expected to be irrelevant for PL measurements using one-photon excitation, because of very high absorption coefficient of Si-nc at 450 nm. In the case of TPL scattering is expected to reduce the thickness of the sample where effective excitation takes place, eventually producing a lower emission intensity.

RESULTS AND DISCUSSION

We show in Figure 1 the experimental open-aperture z-scan trace measured at 120 GW/cm² laser fluence on the Si-nc suspension, together with the theoretical fit obtained using the formula for the normalized transmittance of open-aperture z-scan [9]:

$$T(z) = \sum_{m=0}^{\infty} \frac{1}{(m+1)^{3/2}} \left[-\frac{\beta I L_{eff}}{1 + z^2/z_0^2} \right]^m$$

where β is the two photon absorption coefficient of the sample, I is the laser peak fluence, z_0 is the laser beam confocal range and L_{eff} is the effective thickness of the sample as defined in ref. [8]. In our case L_{eff} was practically coincident with the cuvette thickness, because of the very low linear absorption coefficient of our sample. As shown in the insert in Figure 1, the fitting parameter $\beta I L_{eff}$ is linear versus the incident fluence, confirming a true third-order nonlinearity. Using this linearity we obtain $\beta_{susp} = 10^{-2}$ cm/GW for the suspension, corresponding to a Si-nc nonlinearity equal to $\beta_{Si} = 12.5$ cm/GW. Measurements on pure methanol in the quartz cuvette did not show appreciable two-photon absorption. The measured value of the two-photon absorption coefficient is about ten times larger than the value recently obtained on bulk silicon[15] and one order of magnitude smaller than the value measured on very small Si-nc[7] or porous silicon[16]. Since our sample consists of relatively large nanocrystals (about 6 nm diameter) this result is reasonable. Occurrence of two-photon absorption, and concomitant absence of linear absorption, rule out the possibility of exciting the luminescence by excited state absorption or sequential single-photon absorption.

To discuss the possibility of two-photon excitation of luminescence we can consider the effective absorption coefficient $\alpha_{eff} = \beta I$ for a laser fluence of the order of 100 GW/cm², which is therefore of

the order of 10^3 cm^{-1} . Thus we can reasonably expect to efficiently excite the Si-nc in a relatively thick pressed pellet.

We now devote our attention to the luminescence experiments. The time decay of the luminescence emission at 750 nm excited using the frequency doubled femtosecond laser at 450 nm is shown in Figure 2. After removal of the frequency doubling unit, the sample was excited at 900 nm, and we detected a PL emission with very similar temporal behaviour (Fig.2). To compare the decay dynamics in the two cases we fitted the decay curves with the simple and commonly adopted[17] stretched exponential function $I_{PL} = A \exp\left[-(t/\tau)^{\beta_{decay}}\right]$, obtaining good fits of the experimental data over more than two decades, as shown in Fig. 2. The fitting parameters were almost coincident: $\tau=(40\pm 1) \mu\text{s}$ and $\beta_{decay}=0.64\pm 0.01$ were obtained for excitation at 450 nm and $\tau=(40\pm 1) \mu\text{s}$ and $\beta_{decay} = 0.62\pm 0.01$ for excitation at 900 nm. Thus we can conclude that the emitting states after femtosecond IR and blue excitation are the same, as also confirmed by the emission spectra which resulted to be very similar in the two cases, as it will be shown in the following.

Further evidence that the luminescence observed upon IR femtosecond excitation is due to two-photon excitation is given by the expected quadratic dependence of the PL intensity on the laser pulse energy. In Fig. 3 we report the peak amplitude of the PL waveform at 750 nm versus the incident NIR pulse energy, which was varied by changing the RF power applied to the acousto-optic modulator in the cavity dumper. By fitting the data with the function $A = c \cdot x^m$ we obtain $m=2.1\pm 0.1$ demonstrating true TPL. For comparison we also report in Fig. 2 the luminescence intensity upon excitation at 450 nm. In this case the fit gives $m=1.03\pm 0.03$, as expected for single-photon excitation.

Also, we used the CCD detection setup described in the Experimental part to measure the luminescence spectrum emitted using two-photon and one-photon excitation. The results are reported in Figure 4 for 11 nJ pulse energy at 450 nm and 37 nJ pulse energy at 900 nm. The two spectra are very similar, confirming our previous result on the identity of the emitting states in the

two cases. The small differences could be due to the strongly different excitation density in the two cases, or to the different one- and two-photon absorption coefficient of the nanocrystals populations emitting at different wavelength, i.e., of different core size. Work is in progress to clarify this point.

CONCLUSION

In conclusion we have measured the two-photon absorption coefficient on a Si-nc suspension obtaining a value suitable for two-photon excitation of luminescence. Accordingly we have observed two-photon excited luminescence emission from chemically oxidized pyrolytic silicon nanoparticles, using femtosecond NIR excitation at 900 nm. Comparison with the luminescence emission excited by linear absorption at 450 nm showed the same time dependence and emission spectrum.

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FIGURE CAPTIONS

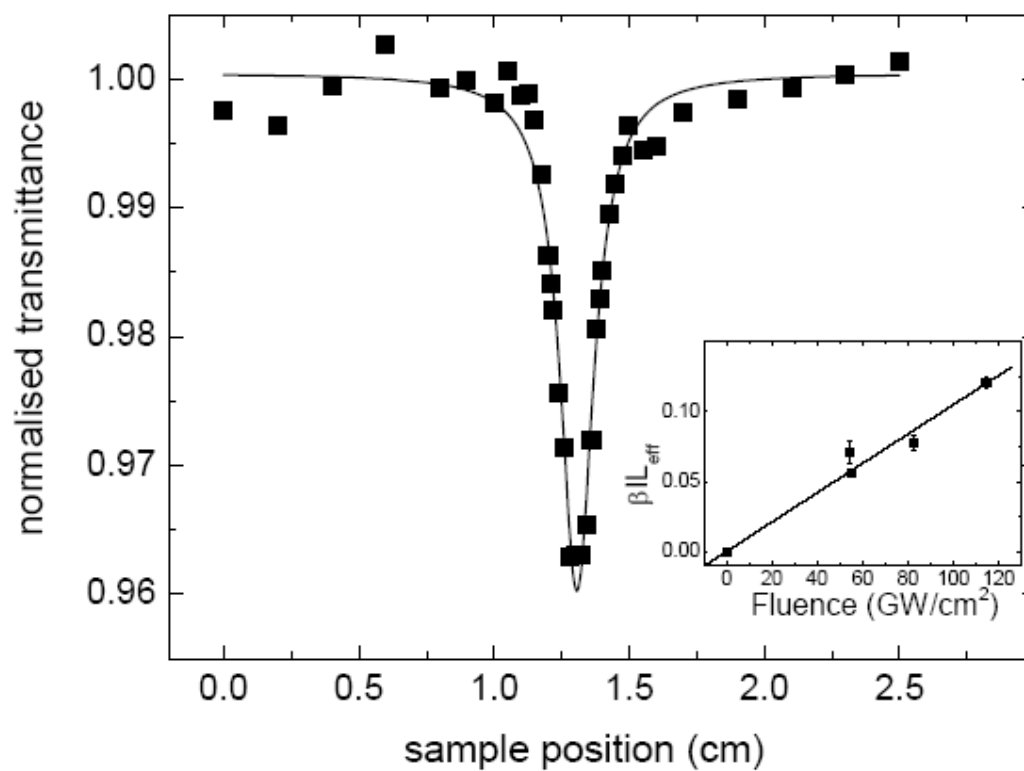
FIGURE 1. Open aperture z-scan measurement on 2g/l Si-nc suspension in methanol and theoretical fit as detailed in the text. Insert: behaviour of the nonlinear parameter $\beta I L_{eff}$ obtained from fit of experimental data as a function of incident fluence.

FIGURE 2. Time decay of the luminescence at 750 nm after femtosecond NIR excitation at 900 nm and blue excitation at 450 nm. Also shown the fits using the stretched exponential function.

FIGURE 3. Peak amplitude of the luminescence emission at 750 nm as a function of the excitation pulse energy at 900 nm and at 450 nm.

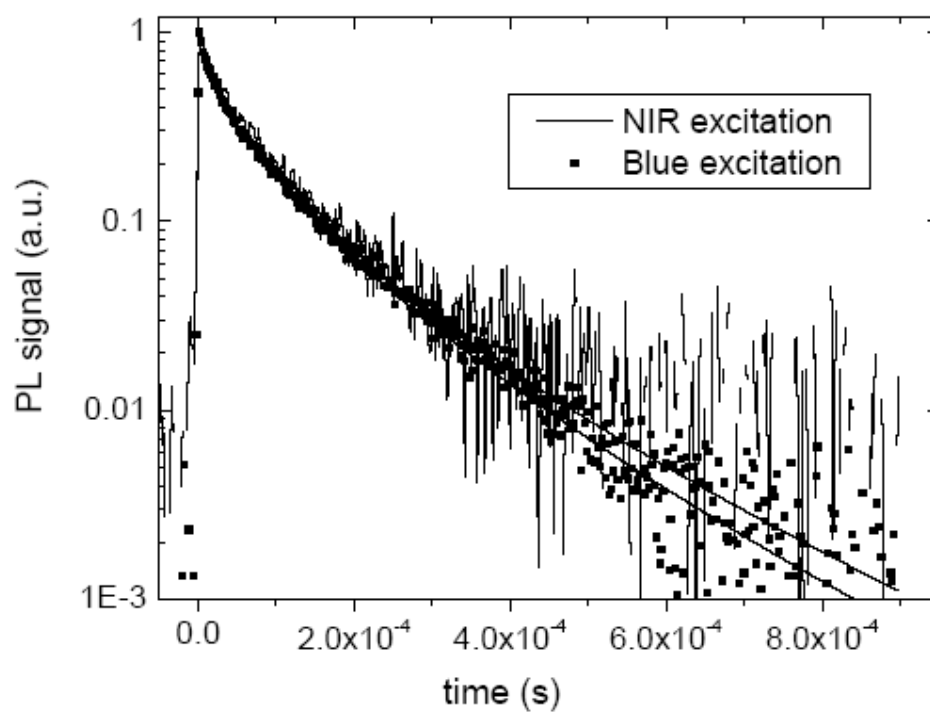
FIGURE 4. Luminescence emission spectrum after femtosecond NIR excitation at 900 nm and blue excitation at 450 nm. The oscillations on top of the bands are an artefact due to low-pass interference filter used to reject the laser excitation.

Fig. 1



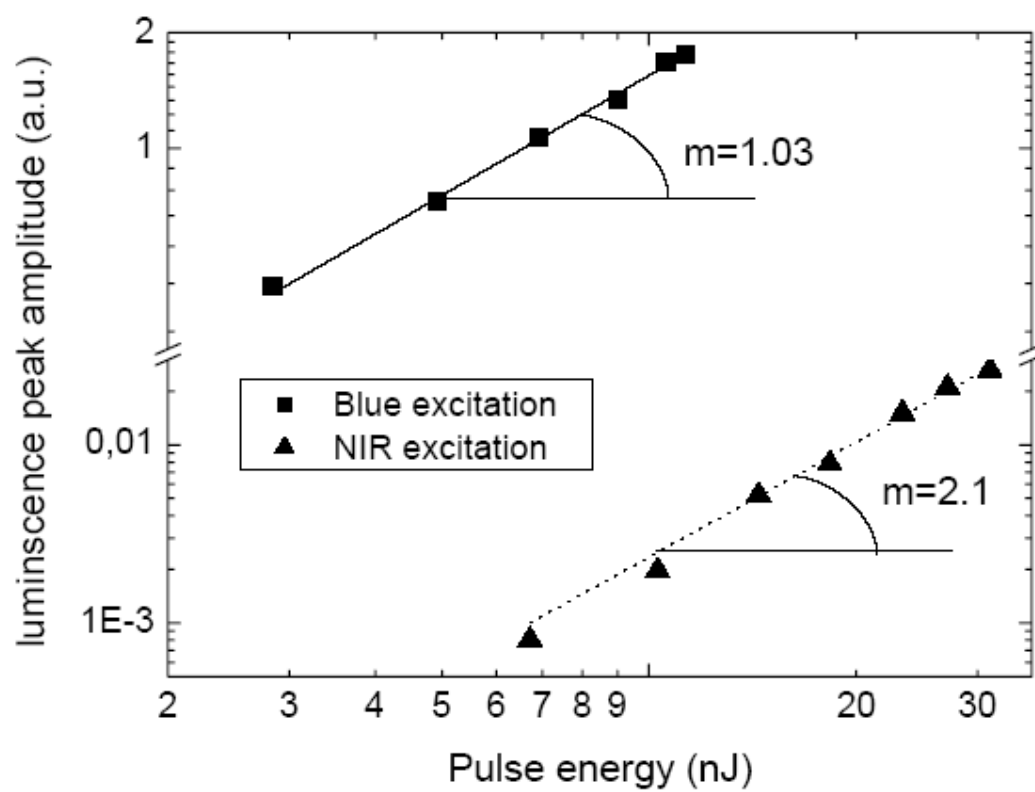
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Fig. 2



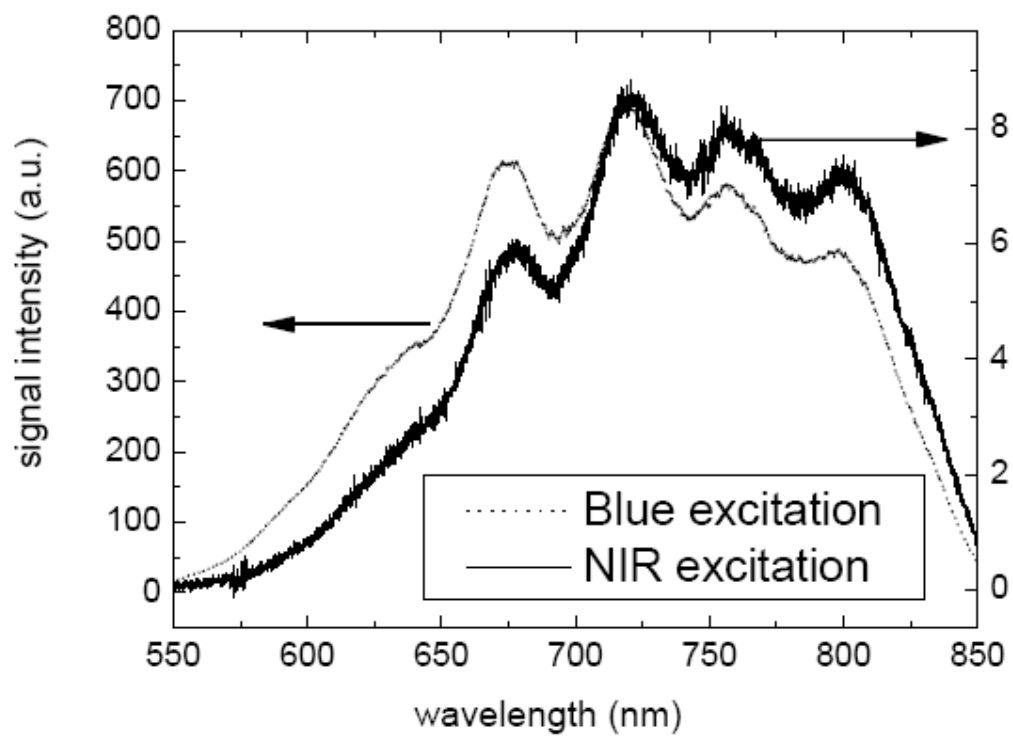
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Fig. 3



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Fig. 4



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