



## Effects induced by UV laser radiation on the blue luminescence of silica nanoparticles

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### ABSTRACT

The effects induced on the blue luminescence centered around 2.8 eV, characteristic of silica nanoparticles, were investigated by monitoring its intensity during and after exposure to the third and the fourth harmonic of a Nd:YAG pulsed laser. The luminescence trend is found to be dependent on the UV photon energy: 3.50 eV photons induce a partial bleaching followed by a recovery in the post-irradiation stage; 4.66 eV photons cause a total bleaching permanent after the irradiation. These results are interpreted as the conversion of luminescent defects towards stable and metastable configurations.

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### 1. Introduction

The high photon emissivity in a wide range, from IR to visible, is one of the most relevant phenomena emerging from the reduction of silica down to nanoscale [1–4]; hence it is promising for the development of optical nanotechnologies (down converters, probes, displays) [5–7]. It is well accepted that the origin of this luminescence is related to the high specific surface of silica nanoparticles ( $\sim 100 \text{ m}^2/\text{g}$ ) [1,2,5,6,8], however, the role of specific optically active centers remains poorly understood. An obstacle to the interpretation of data is due to the huge variety of defects arising from the reactions, at the surface sites, of molecular and atomic species of surrounding atmosphere [9–13]. Nevertheless, a bright photoluminescence (PL) centered around 2.8 eV (blue band), stable in the ambient atmosphere, is usually observed in silica nanoparticles. It can be excited in a wide range, extending from visible to UV, and it is characterized by a fast decay time, in the nanoseconds timescale [8,9,14]. The monotonic increase of its intensity on increasing the specific surface area indicates that it originates from defects localized in the nanoparticles surface shell [15]. The origin of this PL band remains an open question, actually only a model has been proposed: a defect pair consisting of a dioxasilirane,  $=\text{Si}(\text{O}_2)$ , and a silylene,  $=\text{Si}^{**}$  [8]. Recently, it has been demonstrated that this band decreases and red-shifts by addition of  $\text{H}_2\text{O}_2$  or mineral acids (HCl

or  $\text{H}_2\text{SO}_4$ ) [16,17]; whatever the model, these results suggest a possible quenching of the luminescent centers.

In order to gain further information on the structure of the blue luminescent defects, in the present work we have monitored the PL both during and after UV laser irradiation. This approach is useful to investigate the stability of these centers under UV exposure and the induced chemical reactions with atomic or molecular species of the ambient atmosphere.

### 2. Experimental methods

We used samples obtained by commercial fumed silica nanoparticles (Aerosil) supplied in powder form by Evonik-Industries [18]. These materials differ for the specific surface (S) and the average particle diameter (d). In particular, we investigated two typologies of materials: one, named AE300, with  $S=300 \pm 30 \text{ m}^2/\text{g}$  and  $d=7 \pm 1 \text{ nm}$ ; the other, named AE150, has  $S=150 \pm 15 \text{ m}^2/\text{g}$  and  $d=14 \pm 2 \text{ nm}$ . In a previous study performed by atomic force microscopy technique [19], it is shown that the diameters of these fumed silica nanoparticles have a statistical distribution with average values in agreement with that declared by the producer. Silica nanoparticles have been pressed at 300 MPa into tablet of  $\sim 1 \text{ mm}$  thickness.

UV-irradiations were performed at room temperature using the third (3.50 eV) and the fourth harmonic (4.66 eV) of a pulsed Quanta System SYL 201 Nd:YAG laser (pulse width  $\sim 5 \text{ ns}$ , spot size  $\sim 0.4 \text{ cm}^2$ ). The 3.50 eV exposure was done with pulse repetition rates of 10 Hz, 2 Hz, and 1 Hz and energy density of

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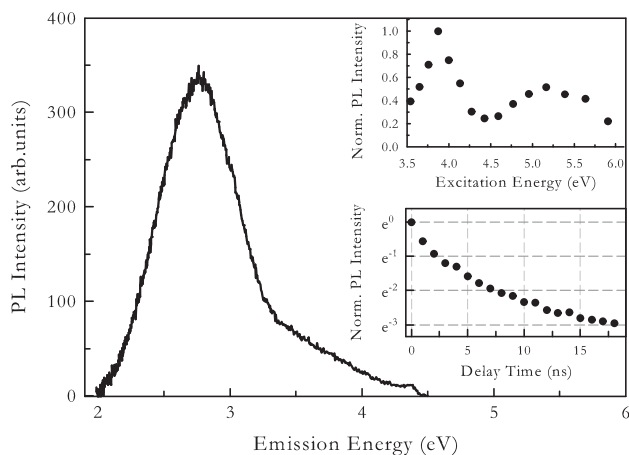
$\Phi_1 = 7.5 \text{ mJ/cm}^2$ ,  $\Phi_2 = 37.5 \text{ mJ/cm}^2$ , and  $\Phi_3 = 75 \text{ mJ/cm}^2$ , respectively, so as to deposit on the sample the same energy density in the same time interval. The 4.66 eV exposure was carried out at 2 Hz repetition rate and 37.5 mJ/cm<sup>2</sup> pulse energy density. The mean power of the laser beam was monitored by a pyroelectric detector and kept constant during each irradiation.

Visible luminescent centers were investigated by ex situ time-resolved PL technique. The PL spectra were performed at room temperature in a standard front-scattering geometry; pulsed light at excitation energy  $E_{exc} = 4.96 \text{ eV}$  (pulse width  $\sim 5 \text{ ns}$ , repetition rate 10 Hz) was provided by a VIBRANT OPOTEK optical parametric oscillator laser system, pumped by the third harmonic (3.50 eV) of a Nd:YAG laser. The pulse energy was monitored with a pyroelectric detector and the fluence/pulse was maintained at  $\Phi = 0.8 \text{ mJ/cm}^2$ , low enough to avoid the generation of any defect. The emitted light was spectrally resolved by a monochromator (SpectraPro 2300i, PI/Acton) equipped with a 150 grooves/mm grating blazed at 300 nm and acquired by an intensified charge coupled device (CCD) camera driven by a delay generator (PI-MAX Princeton Instruments) that sets the time acquisition of the emitted light (gate width  $\Delta T = 200 \text{ ns}$  and time delay  $T_D = 10 \text{ ns}$  after the laser pulse). All the emission spectra were detected with a bandwidth of 20 nm and were corrected for the monochromator dispersion.

### 3. Results

As a representative view, the spectroscopic characteristics of one of the as grown samples (AE150) are reported in Fig. 1. The blue emission is centered around 2.8 eV with full width at half maximum (FWHM)  $\sim 0.7 \text{ eV}$ , its excitation shows two peaks around 3.9 eV and 5.0 eV, its decay occurs in the nanoseconds timescale. These characteristics are in good agreement with previous works [8,9,14]. We also observe a contribution at lower intensity, around 3.5 eV. UV luminescence of high surface silica has been attributed to hydrocarbons contamination [9] or surface silanols (Si-OH) [20], however, in this work we will not deal with it.

Prior to study the effects induced by high power laser radiation, we have exposed for 1 h the samples to UV photons coming from the laser used for the ex situ PL measurements ( $E_{exc} = 4.96 \text{ eV}$ , fluence/pulse  $\sim 0.8 \text{ mJ/cm}^2$ ), up to store a total

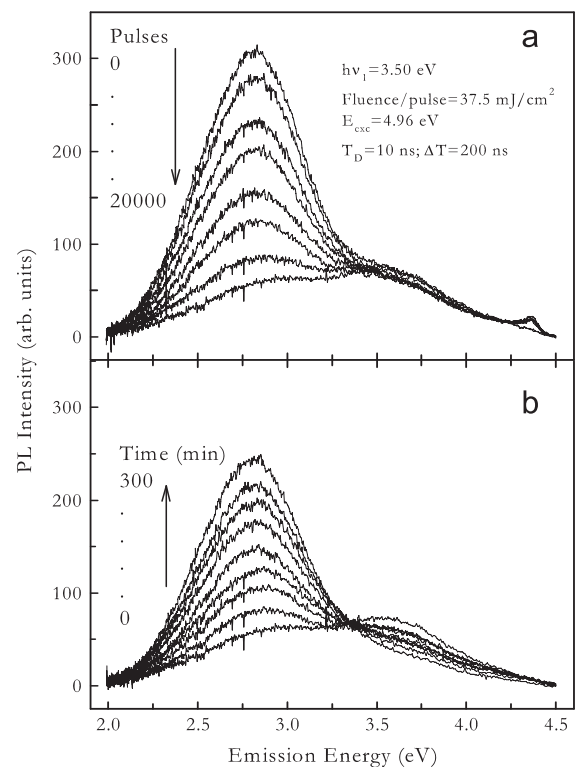


**Fig. 1.** PL spectrum of the as grown AE150 sample excited at  $E_{exc} = 4.96 \text{ eV}$  and acquired with  $T_D = 10 \text{ ns}$  and  $\Delta T = 200 \text{ ns}$ . The insets show, at the top, the excitation spectrum acquired at emission energy  $E_{em} = 2.74 \text{ eV}$ ; at the bottom, the decay time of the blue band peak obtained acquiring the PL spectra with  $\Delta T = 1 \text{ ns}$  and  $T_D$  ranging from 0 to 20 ns.

fluence  $\sim 30\,000 \text{ mJ/cm}^2$ . We observed that this does not cause any variation of the blue band intensity.

Then, we have followed the evolution of the spectral and lifetime features related to the blue band, both during and after irradiation with the third harmonic of the Nd:YAG laser ( $h\nu_1 = 3.50 \text{ eV}$ ). We have exposed our samples to an increasing number of pulses, from 1 to 20 000, with fluence/pulse  $\Phi_2 = 37.5 \text{ mJ/cm}^2$  so as to deposit a total fluence of  $750 \text{ J/cm}^2$ . During the irradiation stage, we performed ex situ time resolved PL spectra under  $E_{exc} = 4.96 \text{ eV}$ . In Fig. 2a we report some representative curves observed in the AE150 sample; as indicated by the arrow the blue band decreases on increasing the number of deposited pulses. The post irradiation trend of the PL spectra, monitored for a time of about 5 h after the last irradiation, is depicted in Fig. 2b. The blue band intensity increases back to its value before irradiation. We note that its spectral features (peak position and FWHM) remain the same both during and after irradiation. In Fig. 3 we report the decay time recorded before, during and after the irradiation. All the curves are described by a stretched exponential, characteristic of luminescent defects embedded in a disordered matrix [12]; we estimate a common lifetime, measured as the time necessary to reduce the intensity by a factor  $1/e$ ,  $\tau = 2.0 \pm 0.3 \text{ ns}$ . We appreciate some differences at longer delay time: the decay rate is faster after a fluence of  $\sim 150 \text{ J/cm}^2$  and after the recovery. The same spectroscopic phenomenology is observed in the AE300 sample.

To quantitatively characterize the bleaching and the recovery of the blue band, its PL intensity is reported in Fig. 4. During the irradiation stage, the PL kinetics is plotted as a function of the fluence in a semilogarithmic scale, while it is plotted versus time in the post irradiation stage, where  $t=0$  corresponds to the end of the irradiation session. In the same graph we show the PL intensities measured in analogous experiments under exposure



**Fig. 2.** Evolution of PL spectra measured ex-situ in the sample AE150 during (a) and after (b) irradiation with  $h\nu_1 = 3.50 \text{ eV}$  and fluence/pulse  $= 37.5 \text{ mJ/cm}^2$ . All spectra are excited at  $E_{exc} = 4.96 \text{ eV}$  and acquired with  $T_D = 10 \text{ ns}$  and  $\Delta T = 200 \text{ ns}$ . The arrows indicate the trend of the blue band.

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