



# Environment assisted photoconversion of luminescent surface defects in SiO<sub>2</sub> nanoparticles



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## ABSTRACT

Time-resolved photoluminescence investigation on SiO<sub>2</sub> nanoparticles was carried out in controlled atmosphere, with the aim to discern the effects induced on the typical blue luminescence band by high power UV Nd:YAG laser photons (4.66 eV) and by some selected molecular species of the air (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O). These factors ultimately determine both the brightness and photostability of the emitting defect, so as to limit the unique and attracting potentialities offered by this system in many applicative fields. Here it is highlighted that the effects due to photons and molecules, singularly considered, are not additive, the radiation being more dramatic in reducing the emission efficiency. Moreover, by analyzing the kinetics to convert the defects in a non-luminescent configuration both by the direct (photon-defect) and indirect (photon-molecule-defect) interactions, the threshold bleaching fluence is derived, ranging between 5000 J/cm<sup>2</sup> (in a vacuum) and 60 J/cm<sup>2</sup> (in air). These results indicate that an outstanding enhancement of the defect photostability is gained by passing from ambient atmosphere to vacuum condition, leading to foresee an immediate and relevant improvement in the field of the single-emitter spectroscopy based on the visible emission of SiO<sub>2</sub> nanoparticles.

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## 1. Introduction

Optical phenomena represent a wide class of physical properties influenced by the size reduction of materials to nanoscale. Depending on the particular system, quantum confinement and/or surface defects are usually invoked to address the experimental evidences. In this respect, silica nanoparticles (SiO<sub>2</sub> NPs) are archetypal in showing emission activity strongly connected with the presence of surface states. A large variety of peculiar photoluminescence (PL) bands, extending from the UV to the Visible spectral range, has been identified [1–6]. Their occurrence is made strictly contingent upon the environmental conditions and only one PL band turned out to be stable at room temperature in ambient atmosphere. This emission is centered in the blue region of the spectrum (~2.8 eV) under UV excitation (from ~3 eV to ~5 eV) and decays in few ns. The attri-

bution of the blue PL to a specific defect is still matter of debate, the most endorsed hypothesis relates it to two faced defects, silylene (Si•• and dioxasilirane (Si(O<sub>2</sub>)), localized on the NPs surface [3].

Whatever the origin, these characteristics are appealing for optical-based applications and keep on motivating the interest towards this material which use, since decades, is already well-established in many technological fields ranging from lighting to photovoltaics and photonics [7–12]. A novel frontier is the single-emitter fluorescence that requires high brightness and photostability when the focused laser pulse impinges on it [12]. Both of these characteristics are limited by the interaction of the luminescent defect with exciting photons and the molecular species in the ambient.

In this context, the purpose to improve and optimize the surface related emission efficiency of SiO<sub>2</sub> NPs passes through the knowledge of the luminescent centers response to external factors, such as radiation and atmospheric conditions, which are unavoidably involved in the emission mechanism. Many works have dealt with the study of the photostability of the blue emitting defects or with their interaction with specific molecular species [4,12–21]. Often, variations in the PL features have been observed and interpreted as bleaching or quenching processes, respectively. Up to now, no

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attempts have been made to disentangle these effects by considering, individually, their relative weight in the PL modifications. With this aim, taking as a reference the PL observed in a vacuum, in this work the combined effects induced by UV laser radiation in controlled atmosphere ( $O_2$ ,  $N_2$ ,  $CO_2$ ,  $H_2O$ ) will be presented. It will be pointed out that the radiation-defects interaction is an environment-assisted process, the effects of the radiation and of the atmosphere, individually considered, being not additive.

## 2. Materials and methods

Aerosil<sup>®</sup> fumed  $SiO_2$  NPs provided in powder form by Evonik-Industries are considered in the present study. Their structural and morphological properties, given by XRD, IR, SEM and TEM characterizations, are reported in the on-line catalog [22]. In particular, particles with specific surface of 90, 150, 200 and  $300\text{ m}^2/\text{g}$  were investigated. In order to obtain self-supporting samples, the powder was pressed at 300 MPa into tablets of thickness  $\sim 1\text{ mm}$ . The obtained tablets were heated in air at  $300^\circ\text{C}$  for two hours to increase the emission intensity in the visible spectral range and to remove any spurious contaminations [23,24].

PL measurements and irradiation in controlled atmosphere were performed placing the sample in a cryostat. A vacuum pump was used to stabilize the pressure down to  $10^{-7}\text{ kPa}$ . Once the vacuum was achieved, by connecting the cryostat to different gas tanks, PL spectra were acquired both in a vacuum and in controlled atmosphere ( $O_2$ ,  $N_2$  and  $CO_2$ ), before and during UV exposure. Moreover, by putting high purity water in a vessel, pre-evacuating and connecting it to the sample chamber, the same measurements under  $H_2O$  atmosphere were performed. In all cases, a fixed gas partial pressure  $\sim 0.1\text{ kPa}$  was maintained in the cryostat.

UV irradiation was performed by pulsed light at photon energy  $E=4.66\text{ eV}$  (pulse width  $\sim 5\text{ ns}$ , repetition rate 10 Hz, spot size  $\approx 3\text{ mm}$ ) provided by the IV harmonic of a Quanta System SYL201 Nd:YAG laser system. The fluence/pulse, monitored with a pyroelectric detector, was fixed at  $\phi_i=140\text{ mJ}/\text{cm}^2$  ( $1.9 \times 10^{17}$  photons/ $\text{cm}^2$ ). The samples were exposed to an increasing number of pulses so as to deposit a total fluence  $\Phi=7000\text{ J}/\text{cm}^2$  ( $9.5 \times 10^{21}$  photons/ $\text{cm}^2$ ).

The emission properties were studied by time-resolved PL technique. Pulsed light at  $E_{exc}=4.66\text{ eV}$  was provided by the same laser system used for the irradiation, taking care to excite the same sample area exposed to irradiation. The excitation fluence/pulse was maintained at  $\Phi=2\text{ mJ}/\text{cm}^2$  ( $2.7 \times 10^{15}$  photons/ $\text{cm}^2$ ), much lower than the irradiation one. The emitted light was spectrally resolved by a monochromator (SpectraPro 2300i, PI/Acton) equipped with a grating with 150 grooves/mm and blazed at 300 nm. The spectra were acquired by an intensified charge coupled device (CCD) camera driven by a delay generator (PI-MAX Princeton Instruments) that allows to set the time acquisition parameters (integration time,  $\Delta T$ , and time delay from the end of the laser pulse,  $T_D$ ). The spectra hereafter reported were detected with an emission bandwidth of 10 nm ( $\sim 0.06\text{ eV}$  in the region of interest around 2.8 eV) and are corrected for the monochromator dispersion. The uncertainty associated to the intensity values ( $\sim 5\%$ ) is mainly due to the laser fluctuations.

## 3. Results and discussion

The results reported in this work consist in singling out, separately, the influence on the blue luminescent defects by high power UV laser photons and selected molecular species, thus understanding their combined effects. To this aim, a bare system is required and therefore the PL observed in a vacuum was taken into account as a reference. It is worth mentioning some general phenomenolog-

ical observations revealed in all the materials under investigation. This is essential to be in line with the characteristics already known in literature and to get some information useful in the ongoing discussion. Under UV excitation at 4.66 eV, all the samples emit in air a PL band peaked around 2.8 eV, with full width at half maximum FWHM  $\sim 0.8\text{ eV}$  and a decay time  $\tau \sim 10\text{ ns}$ . The PL intensity increases on increasing the specific surface of NPs (Fig. S1 of Supporting Information), thus addressing the defects to intrinsic surface states whose origin is strictly related to the bond strains on the surface, which are stronger when the curvature radius of the NPs is decreased [20,25]. On the basis of this finding, the results obtained for the highest specific surface sample will be presented from here on, it being understood that they are general for all types of the materials. After a vacuum treatment ( $P \sim 10^{-7}\text{ kPa}$ ) the spectroscopic features do not change, apart from the intensity increase (Fig. S2 of Supporting Information). These characteristics are consistent with previous works [3,16,19,24,26] dealing with luminescent defects located on the surface of nanostructured  $SiO_2$  and, therefore, in close contact with the molecular species of the environment. From the lifetime, assuming that the 2.8 eV emission is the inverse transition of the 4.66 eV excitation, we roughly estimate the oscillator strength ( $f \sim 5 \times 10^{-2}$ ) or, equivalently, the linear absorption cross section ( $\sigma_{abs} \sim 10^{-17}\text{ cm}^2$ ). Moreover, by comparison with a sample containing a known concentration of surface centers, the surface density of blue luminescent defects emitting in a vacuum results  $\rho \sim 10^{12}$  defects/ $\text{cm}^2$ . A component around 3.5 eV is also evident in the spectrum in air, its intensity being especially remarkable in a vacuum [15,19]. Since this latter contribution is not central in the present work, in what follows we will focus only on the blue PL.

Fig. 1 is an overview of the carried out experiments. The graphs report the PL emitted in a vacuum (a-b),  $H_2O$  (d-e) and  $O_2$  (g-h), before the UV laser irradiation (column (a-g)) and after depositing a total fluence  $\Phi=7000\text{ J}/\text{cm}^2$  in the specific environment (column (b-h)). After stopping the irradiation session and restoring the vacuum, the PL was monitored up to 1 day after (column (c-i)). All the curves are normalized to the vacuum reference condition shown in (a). The same measurements performed under  $CO_2$  and  $N_2$  ambience give similar results to  $O_2$  atmosphere and, for the sake of clarity, are not shown in Fig. 1. The findings here presented can be summarized as follows:

- the interaction of the blue luminescent defect with the molecular species induces a variation of the 2.8 eV peak emission intensity ( $I$ ) respect to the vacuum condition ( $I_v$ ). In particular,  $I$  is enhanced if  $H_2O$  molecules are in the environment ( $I/I_v \sim 1.2$ ) and decreases (*quenching*) in the other cases ( $I/I_v \sim 0.7$  in  $O_2$  and  $CO_2$ ,  $I/I_v \sim 0.9$  in  $N_2$ );
- the PL is drastically reduced through the action of the high power UV photons (*bleaching*),  $I/I_v \sim 0.1$  in a vacuum and  $H_2O$ , whereas in other ambiances  $I/I_v$  is lower than the revealability threshold of the setup;
- after the irradiation, the outcome resulting from restoring the vacuum strongly depends on the irradiation itself: the bleaching is almost permanent (up to 1 day) if it is induced in a vacuum and in  $H_2O$ , whereas the PL is totally recovered (already within 1 h) if the irradiation is performed in the other molecular environments.

The investigation of the lifetime  $\tau$  in the various circumstances clarifies the origin of PL intensity changes. Fig. 2 reports the time decays of the PL monitored at  $E_{em}=2.8\text{ eV}$ , before and after irradiation ( $\Phi=700\text{ J}/\text{cm}^2$ ) performed in a vacuum and in  $O_2$  environment, respectively. All the curves are obtained by monitoring the PL from  $T_D=1\text{ ns}$  to  $T_D=30\text{ ns}$  with  $\Delta T=1\text{ ns}$ , and are normalized to the intensity value recorded at  $T_D=1\text{ ns}$ . Since the decay kinetics in other atmospheres have the same trend as in  $O_2$ , for viewing

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