



Luminescence properties of nonbridging oxygen hole centers at the silica surface

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ARTICLE INFO

Article history:

Available online 18 May 2009

PACS:

73.20.Hb

78.47.Cd

78.55.Mb

78.68.+m

Keywords:

Defects

Nanoparticles

Luminescence

Time resolved measurements

Silica

ABSTRACT

Two variants of the surface-nonbridging oxygen hole center, $(\equiv\text{Si-O})_3\text{Si-O}^\bullet$ and $(\equiv\text{Si-O})_2(\text{H-O})\text{Si-O}^\bullet$, stabilized in porous films of silica nano-particles were investigated by time resolved luminescence excited in the visible and UV spectral range by a tunable laser system. Both defects emit a photoluminescence around 2.0 eV with an excitation spectrum evidencing two maxima at 2.0 and 4.8 eV, this emission decreases by a factor ~ 2 on increasing the temperature from 8 up to 290 K. However, the different local structure influences the emission lineshape, the quantum yield and the decay lifetime. Such peculiarities are discussed on the basis of the symmetry properties of these defects.

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1. Introduction

Study of nano-meter sized silica particles (nano-silica) is a timely research issue strongly motivated by its relevance in modern nanoscale physics and technology. The very high specific surface area of such systems ($\gtrsim 10^2 \text{ m}^2/\text{g}$) favors a large concentration of surface structural defects that play a crucial role in controlling the optical and electrical properties of silica nano-devices [1–4]. One of the most common defects at the silica surface is the oxygen dangling bond or nonbridging oxygen hole center (NBOHC) [5–9] whose structure is denoted by $\equiv\text{Si-O}^\bullet$, where $(\equiv)$ stands for bonds with three oxygen atoms and $(\bullet)$ indicates an unpaired electron. NBOHC is also found in the irradiated bulk silica [10], where assumes a practical relevance because of its absorption bands that dominate both the visible and the ultraviolet (UV) range, all of them being able to excite a photoluminescence (PL) band around 1.9 eV [11,12]. Despite this wide interest, the identification of the optical transitions with the electronic structure of the NBOHC is still debated in the current literature [5,8,13,14]. In this regard, the investigation of surface-defects stabilized by controlled thermochemical processes is advantageous in comparison with the bulk-defect because their structural properties can be fixed *a priori*.

In this work, we report an experimental study on the photoluminescence (PL) properties of two variants of surface-NBOHCs in porous films of silica nano-particles. In agreement with Fig. 1, these variants differ by the structure adjacent to the Si coordination sphere: in the first, $(\equiv\text{Si-O})_3\text{Si-O}^\bullet$, each ligand O is bonded to two Si; in the second, $(\equiv\text{Si-O})_2(\text{H-O})\text{Si-O}^\bullet$, one of the ligand O atoms is terminated by a H. Our purpose is to examine the influence of these specific structures on the spectroscopic features (spectrum lineshape, lifetime and luminescence quantum yield) thus providing a clue to clarify the origin of the optical transitions associated with the NBOHC.

2. Experimental methods

We investigated porous film samples obtained by pressing a highly dispersed Aerosil®-300, a hydrophilic fumed silica with an average particle size of 7 nm, a pore size of 3–6 nm and a specific surface of $\sim 10^6 \text{ cm}^2/\text{g}$. A multi-step thermochemical method was applied to stabilize $(\equiv\text{Si-O})_3\text{Si-O}^\bullet$ and $(\equiv\text{Si-O})_2(\text{H-O})\text{Si-O}^\bullet$ at the hydroxylated silica surface of our samples hereafter named samples 1 and 2, respectively. The main reactions are: (i) surface hydroxyl groups, $\equiv\text{Si-OH}$, are substituted by methoxy, $\equiv\text{Si-OCH}_3$, after treatment in methanol vapor at $T = 700 \text{ K}$; (ii) pyrolysis reactions at $T \geq 1050 \text{ K}$ firstly cause the transformation, $\equiv\text{Si-OCH}_3 \Rightarrow \text{Si-H} + \text{O}=\text{CH}_2$, and (iii) the generation of surface E' centers by breaking $\equiv\text{Si-H}$; (iv) the treatment in N_2O atmosphere

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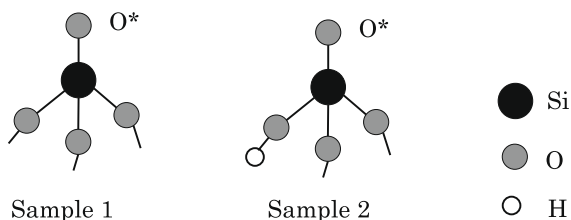


Fig. 1. Structure of the two variants of surface-NBOHC; the O^{*} denotes the dangling oxygen atom.

above 750 K leads to the oxygen chemisorptions thus producing the NBOHCs in the sample 1. NBOHCs in the sample 2 are generated after two further steps: (v) the treatment in H_2 atmosphere at $T = 300$ K leads to the recombination of the first NBOHC variant, the made free H atom reacts with the defect $(\equiv Si-O)_2Si=O$ thus producing an E' center, $(\equiv Si-O)_2(HO)-Si^\bullet$, with a ligand O atom terminated by a H; (vi) the treatment in N_2O atmosphere, similarly to the step (iv), generates the second variant of NBOHC. More details on the manufacturing procedure and on the infrared and EPR measurements used to check the intermediate products are given in Ref. [5]. To avoid any reaction of the surface centers with molecular species, each sample is placed in a pure silica container with a residual He atmosphere of 3–4 mbar.

Excitation over the 1.8–6.0 eV spectral range was provided by a VIBRANT OPOTEK optical parametric oscillator pumped by the third harmonic (3.55 eV) of a Nd:YAG laser (pulse width ~ 5 ns, repetition rate of 10 Hz) and equipped with a nonlinear BKBO crystal for the second harmonic generation. The emitted light was spectrally resolved by a grating with 300 grooves mm^{-1} and 500 nm blaze, the spectral slit bandwidth being set to be 3 nm, and acquired by a gated intensified charge coupled device camera (PIMAX Princeton instruments) within a gate window w_T delayed of t_D with respect to the arrival of laser pulse. All spectra are corrected for the intensity of excitation laser light and for the monochromator dispersion. Temperature was varied in the range 290–8 K by using an Oxford-OptistatCF continuous-flow helium cryostat, equipped with four optical windows and controlled by an Oxford-ITC503 instrument.

3. Results

Fig. 2 shows the spectral properties of the luminescence measured at room temperature in the samples 1 and 2, containing the two variants of the surface-NBOHC. The defect $(\equiv\text{Si-O})_3\text{Si-O}^\bullet$ shows an emission lineshape structured in two sub-bands peaked at 1.92 ± 0.01 eV and 1.99 ± 0.01 eV. The excitation spectrum, measured as the integrated PL intensity, displays two bands: the first asymmetric and centered at 2.02 ± 0.01 eV with FWHM of 0.15 ± 0.02 eV and the second, more intense by a factor of ~ 4 , centered at 4.75 ± 0.05 eV with FWHM of 0.8 ± 0.1 eV and superimposed to a component at higher energies $E_{ex} > 5.5$ eV. The defect $(\equiv\text{Si-O})_2(\text{H-O})\text{Si-O}^\bullet$ exhibits an emission structureless peaked at 1.98 ± 0.01 eV with FWHM of 0.15 ± 0.01 . Also in this case the excitation spectrum consists of two bands, peaked at 2.00 ± 0.01 eV (FWHM = 0.15 ± 0.01) and at 4.75 ± 0.05 eV (FWHM = 0.8 ± 0.1), respectively, the second being more intense by a factor of ~ 15 .

Fig. 3, is reported the temperature dependence of the PL intensity measured in the two samples under excitation at 4.77 eV. Regardless the defect structure, the emission remains almost constant up to ~ 100 K, after that it decreases by a factor of ~ 2 . The PL thermal quenching is fitted by the equation:

$$I_{PL}(T) = \frac{1}{1 + A \exp(-E_g/k_B T)} \quad (1)$$

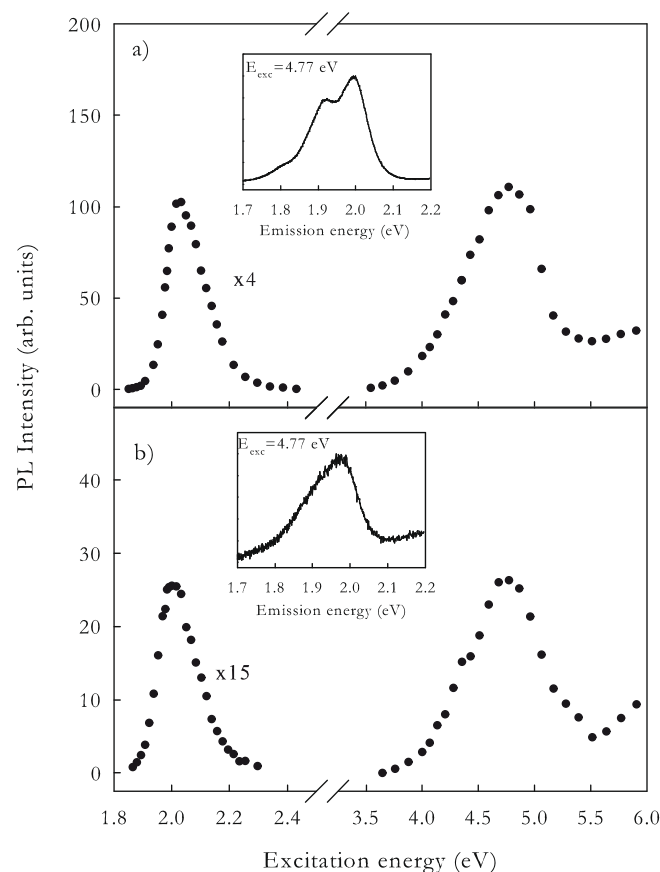


Fig. 2. Emission and excitation spectra measured at room temperature in the sample 1 (a) and sample 2 (b).

where A , E_a and k_B are the preexponential factor, the activation energy and the Boltzman's constant, respectively, in the Arrhenius law accounting for the non-radiative processes that lower the luminescence quantum yield. We get the following best-fit parameters: $A = 10 \pm 3$ and $E_a = 0.05 \pm 0.01$ eV in the sample 1, $A = 15 \pm 3$ and $E_a = 0.07 \pm 0.02$ eV in the sample 2, thus proving that a quite similar non-radiative rate acts in both defects.

Finally, in Fig. 4 we show the PL decay features derived at room temperature by monitoring the intensity at $E_{em} = 1.99$ eV, under excitation at 4.77 eV, with increasing the delay from the laser pulse. Both curves follow a stretched exponential law:

$$I_{PL}(t_D) = \exp[-(t_D/\tau)^\gamma] \quad (2)$$

where τ is the lifetime and γ is the stretching factor that measures the deviation from a single exponential law consistently with a multiexponential decay whose rates are inhomogeneously distributed. These parameters depend on the defect structure: $\tau = 41.2 \pm 0.5 \mu\text{s}$, $\gamma = 0.76 \pm 0.02$ in the sample 1; $\tau = 10.5 \pm 0.3 \mu\text{s}$, $\gamma = 0.72 \pm 0.02$ in the sample 2. We also verified that in both samples the PL decay is weakly dependent on temperature: on cooling from 290 to 8 K, the lifetime increases to $\tau = 52.0 \pm 0.5 \mu\text{s}$ in the sample 1 and $\tau = 12.0 \pm 0.3 \mu\text{s}$ in the sample 2.

4. Discussion

The knowledge *a priori* of the specific structure nearby the silicon coordination sphere allow us to address the observed luminescence features and relate them to the different geometrical properties of each NBOHC variant.

The emission around 2.0 eV observed in the two samples is excited by two different channels: the first is due to the direct

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