β-ray irradiation effects on silica nanoparticles

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Abstract. By electron paramagnetic resonance (EPR) measurements, we examine the amplitude of the signal typically due to a combination of NBOHC (Non Bridging Hole Center) and POR (Peroxy Radical) defects induced by β-ray irradiation (from 1.2 to 1200 MGy) in silica nanoparticles with diameter ranging from 7 to 20 nm. Our data indicate that the signal line-shapes recorded at different doses is quite independent from the particles sizes and from the dose. Furthermore, for each considered nanoparticles size, the concentration of defects is also almost constant with respect to dose, and it does not change significantly if measured after 2 or 9 months from the irradiation. By contrast, we observed that the concentration of NBOHC+POR decreases on increasing the specific surface, indicating that the content of the defects depends on the nanoparticles size. Such dependence can be explained by a shell model in which the detected defects are located in the inner part of the nanoparticles.

1. Introduction

Radiation effects in silica have been investigated by several research groups for different reasons and from different points of view [1-7]. A relevant part of these efforts has been devoted to the understanding of the point defects properties and of their generation mechanisms [1, 8-15]. Among the most important point defects of silica we remind the E′Si center constituted by an unpaired electron localized on a sp^3 orbital of a three coordinated Si atom ($\equiv$Si$^\bullet$ where $\equiv$ stands for the three single bonds with the O atoms, and $^\bullet$ represents the unpaired electron) [1], the Non Bridging Oxygen Hole Center (NBOHC) constituted by an unpaired electron localized on a 2p orbital of a non-bridging oxygen (Si-O$^\bullet$) [1, 8], and the Peroxy Radical (POR) constituted by an unpaired electron located on a pair of oxygen atoms of the structure Si-O-O$^\bullet$ [1, 8, 14]. Because of their paramagnetic nature, all of these defects have been studied by electron paramagnetic resonance (EPR) measurements. Previous investigations characterized the EPR signals of such defects [1, 8, 10] also evidencing that they can be generated by irradiation through different mechanisms involving specific precursors [1, 8, 12-14] or Si-O-Si linkages [1-3]. Furthermore, it was shown that they can be converted into other defects by the reaction with diffusing atoms or molecules [1, 8, 12, 14, 15].

As for other materials, the research on silica has been recently extended also to nanostructures. In this context the study of point defects induced by irradiation has been concerned and the investigation of the E′Si through their EPR signals and other experimental data have evidenced that silica nanoparticles

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can be described by a shell model (surface shell + core) [16-23]. Apropos, until now few information are available for high irradiation doses and for the NBOHC and the POR defects in nanoparticles. For these reasons the present study is focused on the EPR investigation of the NBOHC and POR defects properties and generation in the dose range 1.2-1200 MGy in silica nanoparticles of different average diameters.

2. Experimental

We studied aerosil silica nanoparticles produced by Evonik industries, the particles are produced by oxidation of $SiCL_4$ in O_2/H_2 flame [24, 25]. The specific surface (S) and the average diameter (AD) of each type of nanoparticles have been estimated by the producer by performing BET and TEM analysis. The as-received powders have been pressed in a uniaxial press using a pressure of about 0.3 GPa. In Table 1 we report the name, the specific surface and the average diameter of each investigated type of nanoparticles.

Table 1. Name of the samples, average diameter and specific surface [24,25].		
Sample name	Average Diameter (nm)	Specific Surface (m^2g^{-1})
AE90	20	90 ± 15
AE150	14	150 ± 15
AE200	12	200 ± 25
AE300	7	300 ± 30
AE380	7	380 ± 30

The samples were irradiated with β-rays using a Pelletron accelerator (electron energy 2.5 MeV) at SIRIUS irradiation facility (Ecole Polytechnique, Palaiseau, France). The irradiations were performed at a dose rate of about 18 MGy/h, the minimum dose was of about 1.2 MGy, whereas the maximum one was of 1200 MGy. All the irradiations have been performed in the temperature range 60÷70 °C. We irradiated different samples for each dose. We recorded EPR spectra by standard first harmonic mode with a CW-Bruker EMX-Micro Bay spectrometer, using a microwave frequency of about 9.8 GHz and a 100 kHz magnetic field modulation frequency. The measurements were acquired two and nine months after the irradiation at room temperature.

3. Results and Discussion

No EPR signals are detected in all the investigated samples before the irradiation [20]. In figure 1a, we report the EPR spectrum recorded for the sample AE200 irradiated up to 12 MGy. This measurement evidences the presence of the E′Si at about 3450 Gauss and of the signal of the NBOHC and/or the POR (NBOHC+POR in the following) defects. In the inset of figure 1a, we report a zoom of the most intense part of the signal of the NBOHC+POR, the arrow highlights the amplitude of the signal (Amp) used for the following analysis. To study the line-shape of the EPR signals present in the different samples irradiated at different doses we normalized each spectrum by Amp. A comparison is reported in figure 1b for the sample AE200 irradiated at different doses, and in figure 1c for the spectra recorded at the dose of 171 MGy in the different materials. These data show that the line-shape of the EPR signal is almost independent from the dose and from the sample type. Basing on these results we can suggest that the relative concentrations of NBOHC and POR defects are independent from the sample and from the dose. This finding enables to compare the overall content of NBOHC+POR as a function of the dose and of the specific surface of the nanoparticles in various samples using the values of Amp.
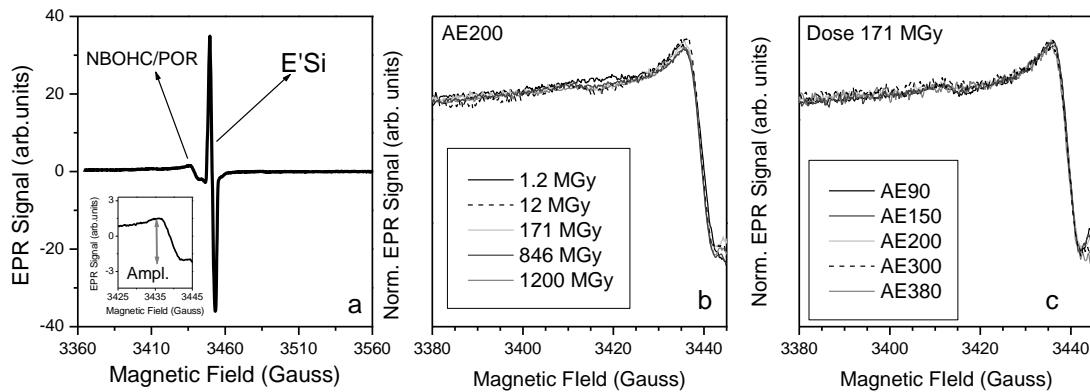
Figure 1. a) EPR spectrum recorded after two months from the irradiation at the dose of 12 MGy for the AE200 nanoparticles; **b)** Normalized EPR signals in the range 3380-3445 Gauss for the AE200 material irradiated at the doses of 1.2 (▬), 12 (---), 171 (▬), 846 (▬) and 1200 MGy (▬); **c)** spectra recorded at the dose of 171 MGy in the AE90 (▬), AE150 (▬), AE200 (▬), AE300 (---) and AE380 (▬) materials.
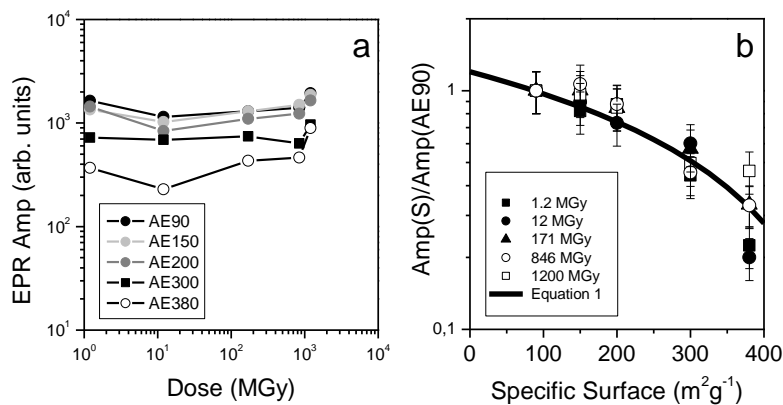

Figure2. a) Normalized EPR amplitude recorded for the samples AE90 (-●-), AE150 (-●-), AE200 (-●-), AE300 (-■-) and AE380 (-○-) as a function of the dose; **b)** ratio Amp (S)/Amp(AE90) at the doses of 1.2 (■), 12 (●), 171 (▲), 846 (○) and 1200 MGy (□), the black line indicates the values calculated by equation 1.

In figure 2a, we report the values of Amp normalized for the experimental conditions and for the samples masses as a function of the dose. The data indicate that for each material the value of Amp is almost independent from the dose suggesting that a saturation concentration value has been attained already at the lowest applied dose. By contrast, we note that the amplitude of the signal depends on the nanoparticles specific surface. More in details, as illustrated by figure 2b, the parameter Amp decreases, independently on dose, with the increase of the specific surface. To compare these results with the previous proposed core shell model [20-23] we evaluated the ratio (Amp(S)/Amp(AE90)) between the Amp measured in the various samples of different specific surface S, and the one measured in the AE90 nanoparticles irradiated at the same dose. Basing on the shell model it is expected that [20, 23]:

$$\frac{Amp(S)}{Amp(AE90)} \approx \frac{Amp^{core}}{Amp(AE90)}\left(1 - \rho_S \times \delta \times S\right) \qquad (1)$$

considering that in general the total EPR signal is given by the sum of the signal arising from the defects located in the core (Amp^{core}) and in the surface shell ($Amp^{surface}$) of the nanoparticle; furthermore, in the model the ratio $\rho_s V_{ss}/m_T$ (V_{ss} being the surface shell volume, ρ_s its density and m_T the total particle's mass) is approximated by the quantity $\rho_s \cdot \delta \cdot S$ (δ being the surface shell thickness and S the specific surface) [20-23]. The line in figure 2b plots the values estimated by eq.(1) inserting $Amp^{core}/Amp(AE90) = 1.2$, $\rho_S = 2.43$ g cm^{-3} (surface shell density [16, 20-23]) and $\delta = 0.8$ nm, which was chosen after fitting the data at each dose. This latter value is slightly lower than the one (about 1nm) previously obtained [20-23], but can be considered in good agreement considering the error bars of the data. In addition, to fit the experimental data, here we assume that the number of NBOHC and POR which are induced in the surface shell are negligible.
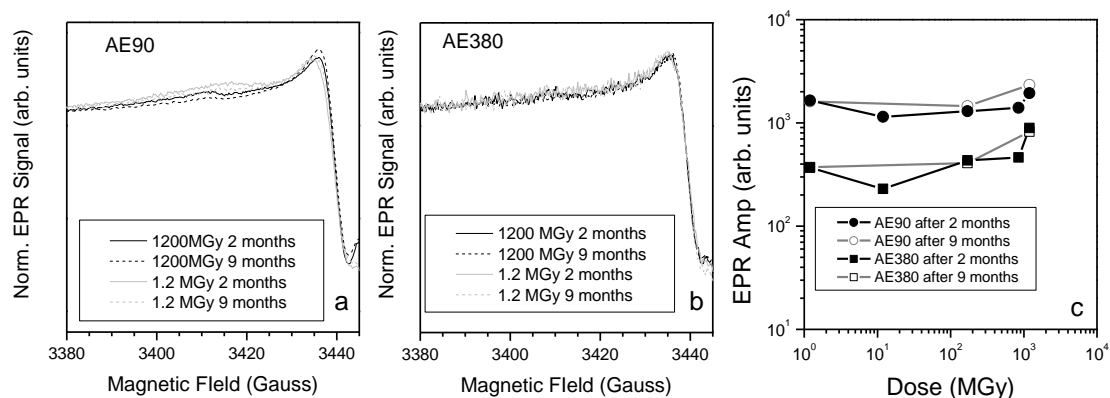

Figure 3. Normalized EPR signals in the range 3380-3445 Gauss data recorded for AE90 (a) and AE380 (b). In both panels (—) spectra acquired 2 months and (---) 9 months after irradiation at 1200 MGy, spectra acquired 2 months (—) and 9 months (---) after irradiation at 1.2 MGy; c) Amplitude of the NBOHC/POR signal as a function of the dose in the sample AE90 after 2 months (-●-) and 9 months (-○-) from the irradiation and in the sample AE380 after 2 months (-■-) and 9 months (-□-) from the irradiation.

For the samples irradiated at 1.2, 171 and 1200 MGy we repeated the measurements about nine months after the irradiation. From the comparison of the spectra reported in figure 3a and b we can guess that the spectra recorded nine months after irradiation show similar lineshape to the ones recorded two months after irradiation. In figure 3c, we compare the signal amplitude recorded for the samples AE90 and AE380 nine and two months after irradiation as a function of the dose. We note that the data are compatible within the experimental error and that for all the investigated materials the larger difference is of about 20% of the amplitude. Basing on this finding, we can consider the defects concentration unchanged.

4. Conclusion

We studied the EPR signals induced in silica nanoparticles by β irradiation up to 1200 MGy, focusing the attention on the signals attributed to NBOHC and/or POR defects. We observed that the signal recorded 2 months after irradiation does not significantly depend on the dose, it does not change significantly if measured 2 or 9 months after the irradiation and that the lineshapes of the signal recorded in different nanoparticles are comparable. By contrast, the signal amplitude depends on the specific surface of the nanoparticles. This latter result is interpreted within the shell model, which describes the nanoparticles as constituted by an inner part were the defects are mainly located and by a surface shell in which the number of defects is negligible.

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