



Sintering process of amorphous SiO₂ nanoparticles investigated by AFM, IR and Raman techniques

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ABSTRACT

We report an experimental investigation on the effects of thermal treatments at different temperatures (room–1270 K) and for different duration (0–75 h) on amorphous silica nanoparticles (*fumed silica*) in powder tablet form. Three types of fumed silica are considered, comprising nearly spherical particles of 40 nm, 14 nm and 7 nm mean diameter. The experimental techniques used here are Raman and infrared absorption (IR) spectroscopy together with atomic force microscopy (AFM). Raman and IR spectra indicate that the structure of nanometer silica particles is significantly different with respect to that of a bulk silica glass. In particular, the main differences regard the positions of the IR band peaked at about 2260 cm⁻¹, the Raman R-band peaked at about 440 cm⁻¹ and the intensity of the D1 and the D2 Raman lines, related to the populations of 4- and 3-membered rings, respectively. Our data also indicate that, under thermal treatments, the structure of fumed silica samples is significantly changed, gradually relaxing towards that pertaining to ordinary bulk silica. These changes are interpreted here on the basis of the morphological information provided by the AFM measurements and assuming a two-shell structure for the fumed silica primary particles.

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1. Introduction

Fumed silica consists in a powder of nonporous amorphous silica nanoparticles produced burning SiCl₄ in H₂/O₂ flame [1–5]. The temperatures used in this aerosol process range from 1370 K to 1570 K. The resulting nanoparticles are almost spherical with mean diameters ranging from few nanometers to few tens of nanometers. In the pristine powder the nanoparticles are not rigorously isolated. They can be partially fused in small groups called aggregates. Moreover, isolated particles and/or aggregates usually form weakly bonded bigger groups called agglomerates. Fumed silica materials are widely employed in industrial processes as additives and are present in a lot of commercial products [4,5]. More recently they have attracted an increasing scientific interest, mainly because they manifest many relevant and fascinating properties, which are essentially related to their nanostructured nature. For example, various experimental results have established that fumed silica nanoparticles have a structure significantly different from that of an ordinary bulk silica glass [1–3]. Furthermore, among the peculiar properties of fumed silica, it has been reported that it is particularly reactive to thermal treatment. In fact, upon thermal treatment at temperatures as low as T = 1250 K the system undergoes a relevant solid phase sintering process [6,7]. Due to this process, after prolonged thermal treatment (typically few hundred hours) the material completely loses its nanostructured nature, looking similar to the ordinary

silica in many aspects. However, in spite of this similarity, the fully sintered samples have been found to manifest interesting and unexpected features. For example, it has been reported that they exhibit a photoluminescence band in the region from 400 nm to 700 nm under ultraviolet excitation at room temperature. This band represents a new and promising feature which could be used in the future to design more efficient optical and displaying devices [6].

Many general properties of the solid state sintering process discussed above have been recently clarified thanks to our experimental investigation performed by Atomic Force Microscopy (AFM) and Raman techniques [8]. To further investigate this topic, here we report new morphologic (by AFM) and spectroscopic (by Raman and IR) experimental data obtained on a variety of fumed silica materials comprising particles with different sizes which were subjected to thermal treatment at different temperatures. The detailed analysis of the collected spectroscopic data and their comparison with the AFM images give strong evidence of a shell-like structure for the primary nanoparticles and allow a more detailed description at a nanometric level of the sintering process induced by thermal treatment in fumed silica.

2. Experimental details

We considered three different types of fumed silica, whose commercial names are Aerosil® OX 50, Aerosil® 150 and Aerosil® 380. In the sample names reported above numbers indicate the specific surface in m²/g. These products differ for the distribution of primary nanoparticle diameters, whose mean values are 40 nm, 14 nm and 7 nm, respectively [4]. The as-received powders were compacted using an

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uniaxial press working at a pressure of 0.3 GPa. It is worth noting that, in accordance with literature data [9,10], this pressure value is unable to induce permanent structural changes in silica nanoparticles. From the self-supporting disks obtained by compacting the pristine powders, the final samples in the form of rectangular tablets with a size of $5 \times 5 \times 2 \text{ mm}^3$ were cut. In particular, a set of 4 samples were produced for each type of fumed silica considered. One of these samples was preserved from any thermal treatment, whereas the remaining three samples were treated at $T = 670 \text{ K}$ for 2 h, at $T = 1270 \text{ K}$ for 2 h and finally at $T = 1270 \text{ K}$ for 75 h.

A bulk $\alpha\text{-SiO}_2$ sample was also considered as a reference to compare the structural properties of fumed silica powders with those of ordinary materials. It consisted in a *Suprasil 1* produced by *Heraeus Quarzglas* with a size of $5 \times 5 \times 1 \text{ mm}^3$.

Tapping mode amplitude modulated AFM [11–15] measurements were acquired with a Multimode V (Veeco Instruments). PointProbe Plus Silicon SPM probes were used, with typical apical diameter of 10 nm. Particular care in assuring the cleanliness of the sample surface is necessary when performing AFM measurements. So we adopted a procedure that consisted in a sequence of three ultrasonic baths in acetone, ethanol and distilled water. Subsequently the samples were positioned in the AFM sample chamber and fluxed with gaseous N_2 for about 10 h. This last step dries the samples, reducing also the thickness of the water film adsorbed on the nanoparticle surfaces.

Raman measurements were acquired at room temperature with a Bruker Ram II FT-Raman spectrometer. The source was a Nd:YAG laser, with a wavelength of 1064 nm and power of 500 mW. The spectral resolution was fixed at 5 cm^{-1} .

IR measurements were acquired at room temperature using a Bruker Vertex 70 Fourier Transform Infrared (FTIR) absorption spectrophotometer, equipped with a MIR light globar source (i.e. a U-shaped silicon carbide piece) and a DLATGS detector. Spectra were acquired with a spectral resolution of 1 cm^{-1} and were averaged over 200 scans. The absorption spectrum of the empty beam line was subtracted from the spectrum of each sample.

3. Results

In Fig. 1 we report the AFM images acquired on the surface of the fumed silica powder tablets obtained as described in the previous section. They represent a $2 \mu\text{m} \times 2 \mu\text{m}$ square portion of the surface, sampled with 512×512 pixels. In these AFM scans the different particle diameters involved in the three fumed silica types here considered are clearly evident. Furthermore, the images also point out that, even if the powders were pressed to obtain self-supporting samples, large voids still remain among the particles or among their aggregate/agglomerate, conferring to the system a significant degree of porosity.

In order to investigate with higher resolution the morphology of the sample surface, we also obtained images acquired on a length scale of $750 \text{ nm} \times 750 \text{ nm}$ sampled with 256×256 pixels, as shown in Fig. 2. The AFM images reported in this figure were acquired on the powder tablets obtained by compacting 7 nm (left column) and 14 nm (right column) nanoparticles. In particular, Fig. 2(a) and (d) refers to untreated samples, Fig. 2(b) and (e) refers to samples thermally treated for 2 h at $T = 1270 \text{ K}$, whereas those of Fig. 2(c) and (f) refers to samples thermally treated for 75 h at $T = 1270 \text{ K}$. These images indicate that thermal treatments of up to 2 h at $T = 1270 \text{ K}$ have no evident effect on the morphology of the sample surface, whereas the situation is radically different for the powder tablets treated for 75 h at $T = 1270 \text{ K}$. In fact, the images acquired on the surface of these latter samples show that thermal treatment has induced the formation of grains of significantly larger mean size than the diameters of the original primary particles. This experimental evidence proves that a relevant sintering process is actually activated in these samples. At variance, in the samples obtained from 40 nm nanoparticles as a starting material, no morphological alterations

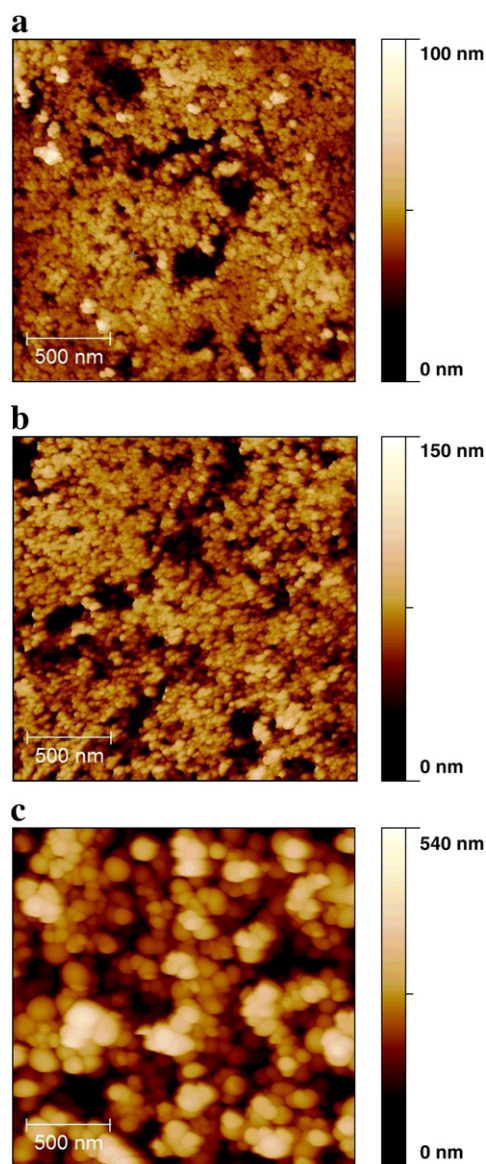


Fig. 1. AFM images acquired on the pristine (untreated) fumed silica powder tablets obtained by compacting nanoparticles with mean diameters (a) 7 nm, (b) 14 nm and (c) 40 nm.

attributable to the sintering process were recognized in any of the considered thermal treatment experiments (data not shown).

As anticipated, to follow the structural changes taking place upon thermal treatment in the three types of fumed silica here considered, Raman measurements were also performed. These data are reported in Fig. 3. In order to make possible a quantitative analysis of the spectra they were normalized to the band at 800 cm^{-1} . This band is assigned to the symmetric stretching of the Si–O–Si groups and it is characterized by the fact that its amplitude and shape hardly change with thermal treatment [16,17]. The data reported in Fig. 3 show that the Raman spectra of the nanostructured samples differ significantly from that of the ordinary bulk silica (also included in the figure, for comparison). Moreover, it is evident that these differences increase on decreasing the mean diameter of the nanoparticles. In particular, two main features are clearly evident. First, the intensities of the D1 (495 cm^{-1}) and D2 (605 cm^{-1}) lines are larger in all the fumed silica samples than in the bulk one, suggesting an enhancement of the number of 4- and 3-membered rings in fumed silica with respect to ordinary materials [3]. Second, the position of the principal band (R-band), assigned to the bending motions of the oxygen atoms in the network, is modified in the

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