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Micro Raman Spectroscopy of Silica Nanoparticles Treated with Aminopropylsilanetriol

V. Volovšek,[1] K. Furić,[2] L. Bistričić,[3] M. Leskovac[1]*

Summary: Micro Raman spectroscopy was used to investigate the structures formed at the surface of amorphous pirogenic silica Aerosil 200. Nanoparticles were treated with 25% water solution of aminopropylsilanetriol and dried in laboratory atmosphere and under vacuum of about 5 mbar. Spectra of pure silica nanoparticles and treated nanoparticles were recorded in the frequency range 20–1700 cm^{-1} and 2500–3800 cm^{-1}. Comparative analysis reveals the existance of different structures formed at the surface of silica nanoparticles depending on drying conditions.

Keywords: aminopropylsilanetriol; hydrogen bonds; Raman spectroscopy; silica nanoparticles; vacuum

Introduction

Amorphous pirogenic silica Aerosil 200 is frequently used as a nanofiller for rubbers and different plastics. It reduces the sedimentation rate, strengthens the elastomers and disperses well in polymeric matrices. Silica nanoparticles have silanol groups at the surface and siloxane bonds inside the particles. The SiOH groups at the surface of the neighboring particles interact through hydrogen bonds creating three dimensional lattice like structure. In order to get hydrophobic silica and to prevent nanoparticles to interact among themselves their surface is frequently modified with organosilane compounds. Vibrational spectroscopies are powerful methods used in investigation of various structures formed at the surfaces of different inorganic particles. Shimizu et al.[1,2] used Raman scattering to study the interaction of 3-aminopropyltriethoxysilane on silica gel and DRIFT spectroscopy to investigate the effect of adsorbed water in the same samples.[3] In this work we studied the effect of the low pressure on the structures of aminopropylsilanetriol (APST) formed at the surfaces of silica nanoparticles. The APST molecules are stable only in the presence of water which prevents forming of siloxane (Si–O–Si) bridges. During the solidification of APST under vacuum, water molecules are being constantly removed from the surrounding as well as from the inside of the sample where they are created in the process of silanization. Therefore, we expect that the structures formed at the surface of nanoparticles will depend on the atmospheric conditions (underpressure) applied.

Experimental Part

Amorphous pirogenic silica Aerosil 200 was purchased from Degussa Company and was used without further purification. According to the specification of the producer the mean diameter of the investigated particles of pure Aerosil was 12 nm and specific surface was 200 m^2/g. 25% water solution of APST was purchased from ABCR Company. Silica nanoparticles were mixed with APST solution and the

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[1] Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev trg 19, 10000 Zagreb, Croatia
Fax: (+385) 01 4597135;
E-mail: volovsek@fkit.hr
[2] Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia
[3] Faculty of Electrical Engineering and Computing, University of Zagreb, Unska 3, 10000 Zagreb, Croatia

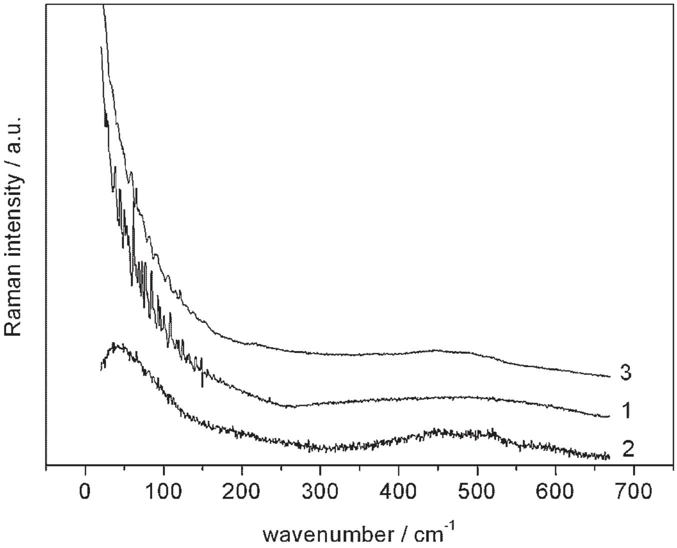

Figure 1.
Low frequency Raman spectra of 1 = pure nanoparticles, 2 = nanoparticles with APST dried in the air, 3 = nanoparticles with APST dried under vacuum.

part of the mixture was dried in the air, while the other part was placed in PVC vessel, connected to the vacuum pump and finally dried under low pressure of around 5 mbar. Raman spectra of pure nanoparticles (sample 1), nanoparticles with APST dried in the air (sample 2) and nanoparticles with APST dried under vacuum (sample 3) were then recorded on Horiba Jobin Yvon T64000 instrument equipped with the Olympus open microscope stage and CCD Symphony detector. Spectra were taken with notch filter in single mode in the frequency region from 700–1700 cm^{-1} and from 2500–3800 cm^{-1} with spectral resolution of 3.5 cm^{-1}. During the acquisition of spectra below 650 cm^{-1}, spectrometer was operating in triple subtractive mode. The 514.5 nm line of a Coherent INNOVA-400 argon ion laser was used for excitation with laser power of 20 mW at the sample place.

Results and Discussion

Comparison between Raman spectra of the two treated Aerosil samples reveals significant differences. In the low frequency region (Figure 1), the spectrum of nanoparticles treated in the laboratory atmosphere (sample 2) shows pronounced Bose band with maximum at 41 cm^{-1}. It represents acoustic modes of the sample which are becoming active in Raman spectrum due to the break-down of selection rules in amorphous materials. Its existence is obviously not related to the nanoparticles because it is missing in the spectra of the pure Aerosil (sample 1). Very similar low frequency spectra were recorded on APST polymer film[4] indicating the existence of medium range order.

In the spectral range from 700–1700 cm^{-1} (Figure 2) there are also few distinctions between the Raman spectra of the three samples. The noise level in the spectra 1 and 2 is much higher compared to the spectrum 3, although all three spectra were recorded under the same conditions. This noise is caused by high fluorescent background which was subtracted in order to compare all three spectra in the same figure. The probable source of this high fluorescence is in the larger amount of pore water incorporated in nanoparticles as well

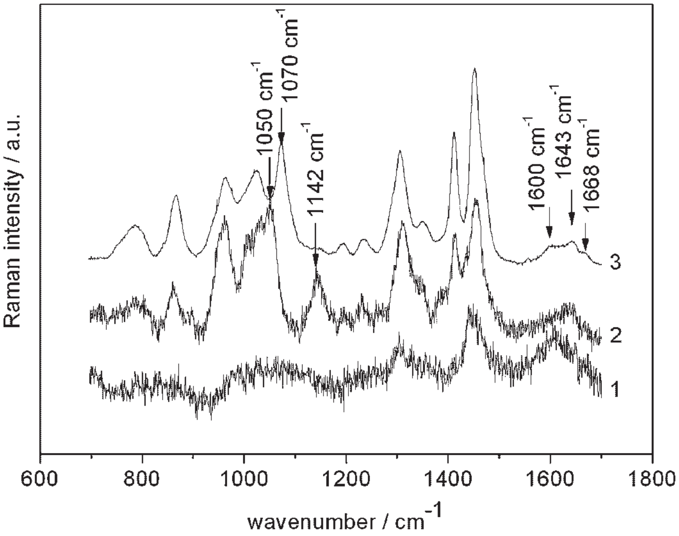

Figure 2.
Raman spectra of 1 = pure nanoparticles, 2 = nanoparticles with APST dried in the air, 3 = nanoparticles with APST dried under vacuum.

as in the mixture of nanoparticles and APST. When this mixture is subjected to high vacuum, water is extracted by rapid pumping, leaving only small amounts of water molecules forming strong hydrogen bonds with silica and APST.

Sample 2 generates bands at 1050 cm^{-1} and 1142 cm^{-1} which are missing in sample 3. Instead, in sample 3 the band at 1070 cm^{-1} is detected. Shimizu et al.[2] in their Raman scattering study of polyaminopropylsiloxane recognized the bands at 1053 cm^{-1} and 1074 cm^{-1} to be sensitive on the concentration of APST in aqueous solution and are useful as the indicators for investigation of the conformations of aminopropyl segments. Our DFT calculations of conformational stability and vibrations of aminopropylsilanol molecule ascribe these bands to mixed CH_2 and NH_2 rocking vibrations in *trans* and *gauche* conformations of aminopropyl chains, respectively.[6] Medium strong Raman band at 1142 cm^{-1} in the spectrum of sample 2 is characteristic for the in phase Si–O–Si vibrations in the rungs of the ladder structures[5] of polyaminopropylsiloxane. It indicates the creation of siloxane bonds among APST molecules and not between APST and substrate nanoparticles.

Another difference arises in the region of NH_2 scissoring vibrations around 1600 cm^{-1}. The APST molecule can form different kinds of intramolecular and intermolecular hydrogen bonds giving rise to slightly different vibrational frequencies. The DFT calculation of APST molecule helped us to assign the band at 1600 cm^{-1} to NH_3^+ bending vibration of hydrogen bonds of the type $SiO^- \cdots H–NH_2^+$ in the *gauche* conformation, and band at 1643 cm^{-1} to NH_2 scissoring mode[6] involved in the inter- and intramolecular hydrogen bonds of the type $SiO–H \cdots NH_2$. The third band at 1668 cm^{-1} might be attributed to OH bending vibration of water molecules involved in hydrogen bonds.

Shimizu et al.[3] investigated DRIFT spectra of 3-aminopropyltriethoxysilane layer modified onto the surface of silica gel. They also found differences in this part of the spectrum and they ascribed them to a marked variation in the environment of amino groups.

The broad Raman bands in the 2800–3000 cm^{-1} region (Figure 3) are assigned to

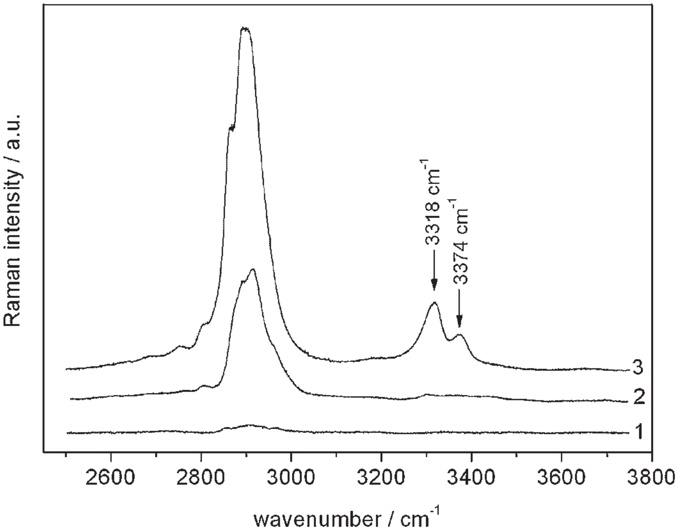

Figure 3.
High frequency Raman spectra of 1 = pure nanoparticles, 2 = nanoparticles with APST dried in the air, 3 = nanoparticles with APST dried under vacuum.

the CH_2 stretching vibrations of the propyl segment.[6] There are some differences in the shape of these bands that can be attributed to different environment of the CH_2 groups in the *trans* and *gauche* conformations of the aminopropyl chains. In the high frequency region the bands at 3318 cm^{-1} and 3374 cm^{-1} assigned to the NH_2 symmetric and asymmetric stretching have much higher intensities in the spectra of nanoparticles treated under vacuum. According to Björnström et al.[7] dehydration process of silica gel induced by thermal treatment is manifested by elongation of SiO–H bonds of the acidic silica groups and dramatic downshift of OH stretching frequencies from $\sim$3600 cm^{-1} to $\sim$3000 cm^{-1} depending on the number of water molecules involved. At sufficiently low water contents, water molecules are forming stronger hydrogen bonds with the silanol groups.

All the characteristic vibrations with suggested assignment are listed in Table 1.

Table 1.
Characteristic vibrations for different structures of polyAPST

ν_{exp}	ν_{calc}	Assignment	Structure
cm^{-1}	cm^{-1}		
1050	1038	NH_2 rock	*trans*
1070	1064	NH_2 rock	*gauche*
1141	1142	Si–O–Si str	ladder
1600	1596	NH_3^+ bend	*trans, gauche*
1643	1619	NH_2 sciss	*trans, gauche*
1669		OH bend	
3318	3351	NH_2 str	*trans, gauche*
3374	3427	NH_2 str	*trans, gauche*

Conclusion

Present investigation of silica nanoparticles treated with aminopropylsilanetriol reveals significant influence of the vacuum drying on the structures formed at the surface of the nanoparticles. Both substances involved in the process have great affinity towards creating different hydrogen bonds between themselves as well as with the water molecules in their surroundings. Applied underpressure of about 5 mbar removes water molecules from the surrounding air, but also from the inside of the mixture. This condition favors the formation of stronger hydrogen bonds. When the underpressure is applied, disordered structure is detected in which propyl chains are predominantly in the *gauche* position and where zwitter-ionic structure of the type $SiO^{-}\cdots H–NH_2^{+}$ is created.

When the mixture is dried under normal pressure lot of water still remains in the sample forming droplets of pore water. Under these conditions the APST molecules are forming partially ordered ladder-like structures (Bose band, band at 1142 cm^{-1}) with aminopropyl chains in the *trans* positions.

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