

Electronic Supporting Information

SiO₂ Nanoparticles as New Repairing Treatments toward the Pietraforte Sandstone in Florence Renaissance Buildings

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Experimental section

Characterization of SiO₂ nanodispersion: particle size distribution and Z potential

To address the particle size distribution and the Z potential measurements (f/mV) two distinct instruments have been used: a Zetasizer Nano ZS analyzer (Malvern, UK) equipped with a backscattering detection mode (with an angle of 173°); and a laser He-Ne operating at 633nm (Laser Doppler Velocimetry). SiO₂ nanoparticles were sonicated in distilled water for 30 minutes, and the original dispersion (1 mg mL⁻¹) was diluted to the final concentration of 0.01 mg mL⁻¹.

Ultrastructural Characterization of SiO₂ nanodispersion: Transmission electron microscopy/energy-dispersive X-ray spectroscopy

Transmission electron microscopy/energy-dispersive X-ray spectroscopy. For transmission electron microscopy observation, the SiO₂ nanodispersion was prepared as follows: a small amount of SiO₂ nanoparticles was resuspended in 1mL of distilled water in a glass tube and then sonicated for 1 h; as the sonication ended, 100 mL of the suspension were immediately deposited on a formvar-coated copper grid, by drop-casting, let dry on absorbent paper and observed under a Zeiss EM 10 transmission electron microscope (Zeiss, Germany) at 60 kV. Transmission electron microscopy (TEM) images were processed by image analysis Fiji software with the tool “Analyze particles.” Measurements were then statistically evaluated by MedCalc Statistical Software version 19.5.1 (MedCalc Software, Ostend, Belgium).

Characterization of deposited SiO₂ nanoparticles by different techniques

The following techniques have been used: X-ray diffraction (XRD), energy-dispersive X-ray fluorescence (XRF), Raman spectroscopy, Fourier transform infrared spectroscopy, Thermal analysis, Scanning electron microscopy/energy-dispersive X-ray spectroscopy.

To determine the presence of SiO₂ nanoparticles, their structure, and crystallinity, X-ray diffraction (XRD) a θ-2θ X'Pert PRO Phillips diffractometer (20°–60° 2θ range) using Cu Kα radiation operating at 40 keV and 20 mA was used.

In order to determine sample composition, energy-dispersive X-ray fluorescence (XRF) was used through a Bruker AXS instrument (#T3S2731; Bruker Kennewick, WA, USA). This apparatus is equipped with a 4W rhodium anode and a

Bruker Xflash SDD with 2048 channels. The spectra were acquired at operating conditions of 15 keV, an anode current of 25 μ A, and no filter for 180 s per assay. By comparing the X-ray radiation to the values for the calibration curves, metal concentrations were determined.

Raman measurements on SiO_2 nanoparticles as solid powders placed on a glass slide have been carried out by a DXR2xi Thermo Scientific Raman Imaging spectrometer. The instrument was equipped with an electron-multiplying charge couple device detector and a solid-state laser with an emission wavelength of 532 nm as a light source. The operating conditions were: excitation power of 5 mW, and the laser was focused on the sample through a 50 x long focal distance objective. The diffused signal was collected with the same objective in a backscattering configuration. The spectral resolution was 4 cm^{-1} (full range grating with 900 lines mm^{-1}).

The Fourier transform infrared (FTIR) spectroscopy was made in transmittance mode on samples in KBr pellets using a Shimadzu Model Prestige 21 spectrophotometer.

Thermogravimetry (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and digital tracking calorimetry (DTC) were performed using a Netzsch Model 449 C instrument equipped with a high-temperature furnace. Samples were placed in a Pt crucible, heated to 500 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ and to 1200 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C min}^{-1}$. Dry air flowed over the samples at 0.070 L min^{-1} . The TG and DSC signals were corrected by subtraction of appropriate baselines.

To perform elemental mapping analysis of SiO_2 nanoparticles for silicon and oxygen by Energy dispersive X-ray (EDX) the sample was prepared as follows. A small amount of SiO_2 nanoparticles was resuspended in 1 mL of distilled water in a glass tube and then sonicated for 1 h; as the sonication ended, 100 mL of the suspension were immediately deposited on a 200 mesh Formvar film Cu grids (Ted Pella, USA) by drop-casting, let dry on absorbent paper and sputter-coated with platinum (Emitec K550 sputter coater) at 15 mA for 1.5 min. SEM analysis was carried out using a Hitachi SU3500 variable pressure scanning electron microscope operating at 15–20 kV in a high vacuum.

Results and discussion

The SiO_2 nanodispersion characterization results

The first characterization concerned the SiO_2 nanodispersion was performed as it was directly applied to the stone, in the restoration site. The nanodispersion (without a solid precipitate appearing in the test tube) lasts in a stable form for over 6 months. The characteristic of nanodispersion's long-lasting stability at room temperature conditions is an important parameter because the nanodispersion can be prepared in advance (and in another place) and then used at the restoration site in a time frame compatible with commercial timelines. In **Figure S1 (a-c)**, the dynamic light scattering study of SiO_2 nanodispersion in distilled water is illustrated together with TEM analysis. The average diameter of the particle size distribution was about 20 nm and the Z-potential value/ ζ of -20.4 mV for SiO_2 nanodispersion. The average particle size diameter measured by TEM (**Figure S1b, c**) was higher at 80 nm. The different values may be due to nanoparticle aggregation, occurring during solvent evaporation caused by TEM technique. In DLS, all measurements are performed directly in the liquid phase. The results of these analyses show that the dispersed nanoparticles are stable and maintain the same size, which is important to establish the reliability of the solution as a conservative agent. If the nanoparticles have a constant size, the result of the restoration process will be homogeneous.

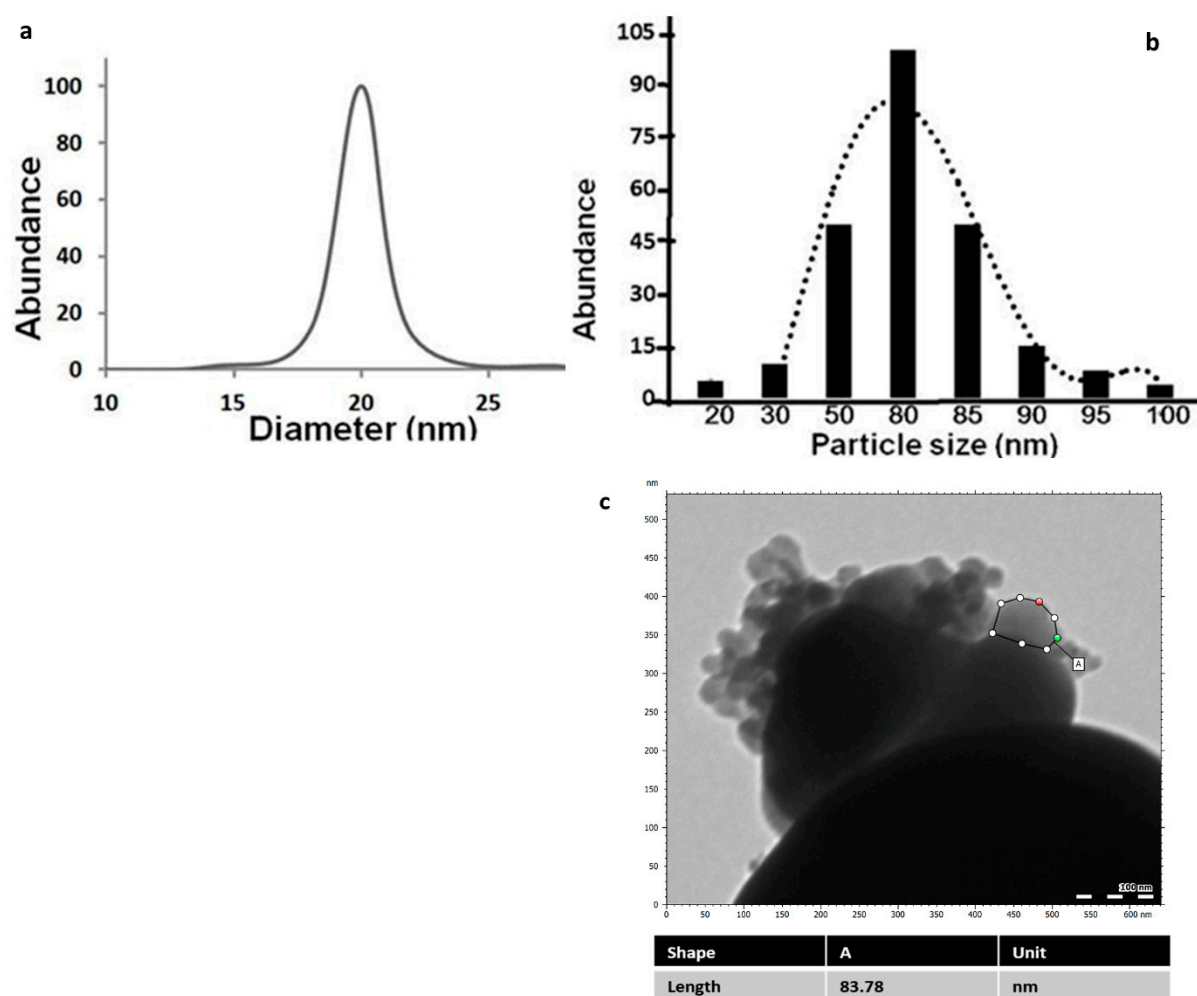


Figure S1. Characterization of the SiO₂ nanoparticle suspension in distilled water: (a) DLS plot and (b) particle size distribution obtained by TEM (micrograph shown in c).

Following the nanodispersion characterization, we focused on the analysis of the newly synthesized nanoparticles in the form of solid powder. The XRD pattern of the synthesized SiO₂ nanoparticles, as shown in **Figure S2A**, reveals a broad peak related to amorphous silica nanoparticles with maximum at about $2\theta=23^\circ$, with (101) Miller indices [32]. The ED-XRF profile of SiO₂ nanoparticles is illustrated in **Figure S2B**, where it is clearly visible that the only detected element is Si at 1.74 keV emission line. The presence of other elements whose shorter peaks are visible is associated with the air (Ar) and the sample holder (Ca) contributions. The Raman spectrum of the SiO₂ nanoparticles is provided in **Figure S2C**. It is composed of two main bands centered at about 527 cm^{-1} and 494 cm^{-1} . The first one is associated with silicon–silicon vibrations, and it is slightly shifted with respect to that of bulk silicon crystal, which is centered at about 520 cm^{-1} , due to the reduced nanoparticle size [33], whereas the band at 494 cm^{-1} represents the typical silicon dioxide/SiO₂ compound spectral signal [34]. In the FTIR spectrum shown in **Figure S2D**, the broad band centered at about 3429 cm^{-1} can be assigned to the hydroxyl groups (ν stretching mode), probably responsible for the hydrogen bonding interactions, providing better dispersion of the SiO₂ nanoparticles [35]. The band centered at 1110 cm^{-1} is assigned to the Si-O-Si asymmetric stretching vibration (ν_{as} mode). Bands around 960 cm^{-1} correspond to the asymmetric bending (δ_{as} mode) and stretching (ν_{as} mode) vibration of Si-OH and the band at 802 cm^{-1} is assigned to O-Si-O bending vibration mode [36].

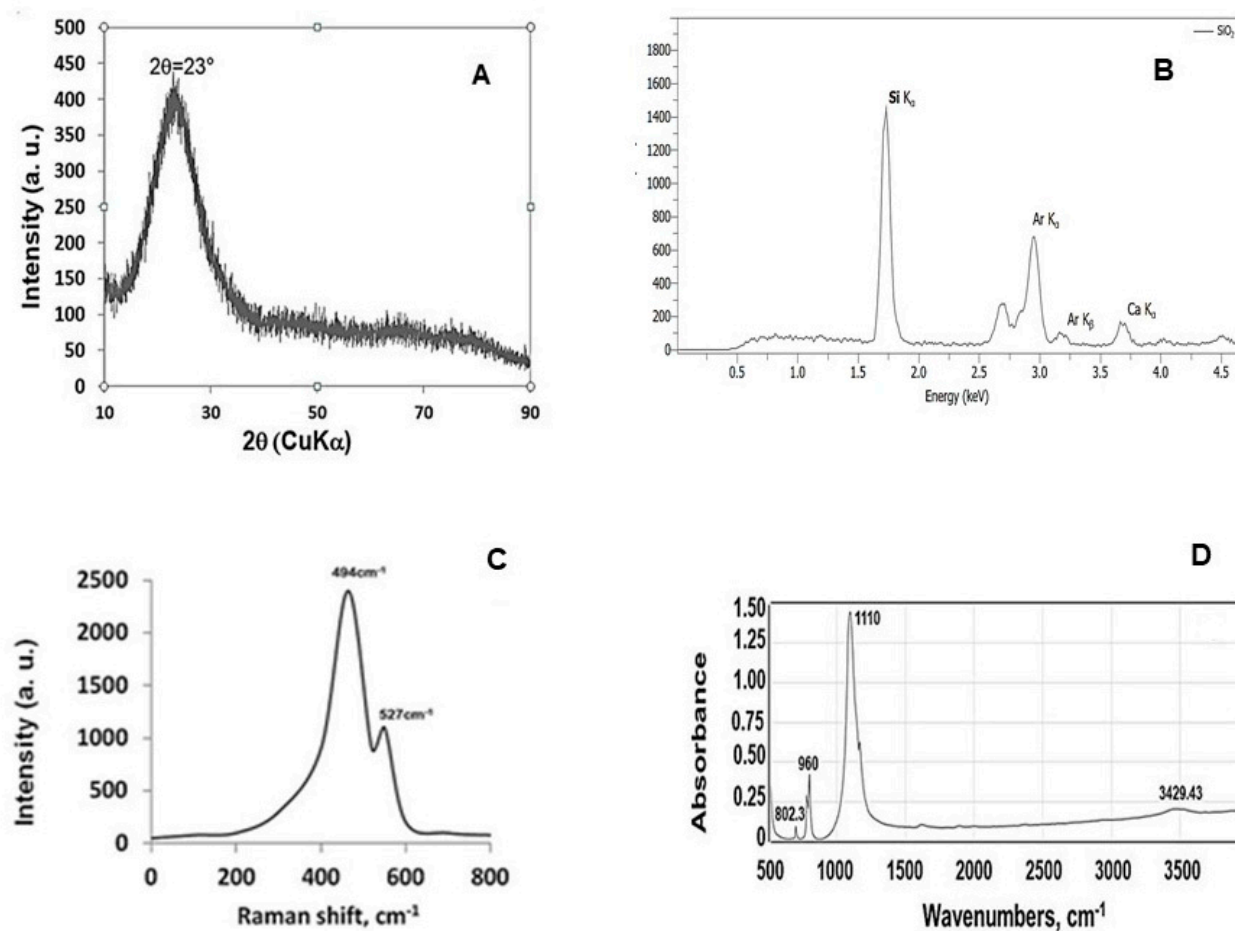


Figure S2. Patterns and spectra of synthesized SiO₂ nanoparticles. (A) XRD. Peak labels: (B) XRF. (C) Raman. (D) FTIR.

As highlighted in **Table S1**, the FTIR spectrum of SiO₂ in Figure 2d has all bands that characterize the SiO₂ species. The indicated band assignments closely match those in the literature [37].

Table S1. FTIR band assignments.

Wavenumber (cm ⁻¹)	Vibrational mode
3429	ν (Hydroxyl groups stretching mode), Si-O-H
1110	ν _{as} (asymmetric stretching vibration mode), Si-O-Si
960	δ _{as} (out of plane bending) and stretching (ν _{as} mode), Si-OH
712	ν ₄ (doubly degenerate planar bending), O-C-O in-plane deformation
802	δ _{as} (bending vibration mode) O-Si-O

The full characterization of SiO₂ nanoparticles by thermal analysis is presented in **Figure S3**. DTA thermogram showed an intensive endothermic peak in the range of 30–150°C and a shoulder at temperatures beyond 300°C. These peaks are correlated to the loss of physically adsorbed water from the surface (5.2%) and chemically adsorbed water bonded to Si-OH (1.3%) through hydrogen bonds, in agreement with the previous FTIR results [35]. The total weight loss of silica material obtained by TG analysis is 6.5%.

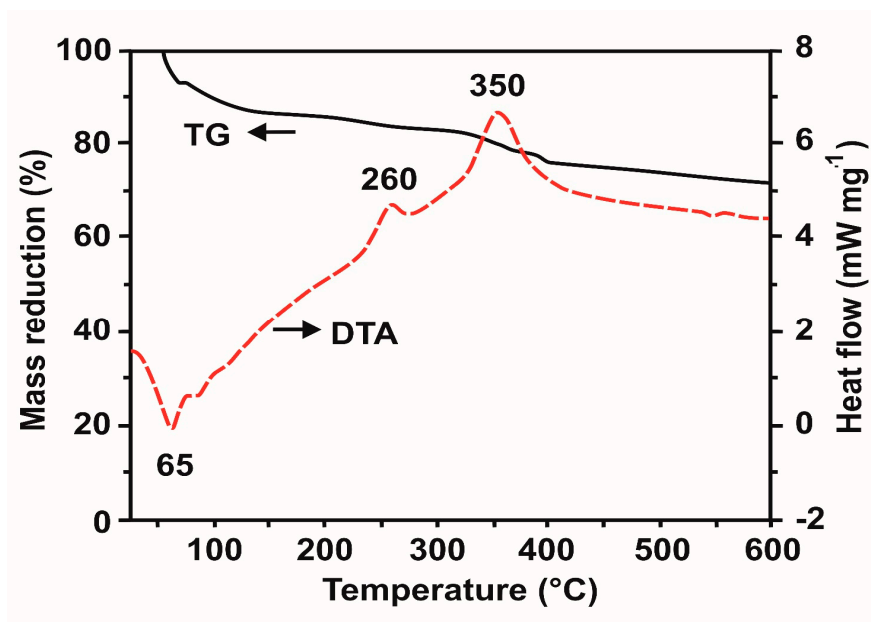


Figure S3. Thermal analysis for SiO₂ nanoparticles. TG-DTA curves.

Figure S4 illustrates the morphological characterization of the synthesized SiO₂ nanoparticles by SEM-EDX. As visible in **Figure S4a**, SEM image shows two aggregations of SiO₂ nanoparticles that form morula-like microcrystals having an oval shape with slightly pointed endings. Red circles target the area analyzed by EDX, whose results are shown in **Figure S4b**. EDX analysis confirmed the chemical composition of nanoparticles as formed by only silicon and oxygen elements.

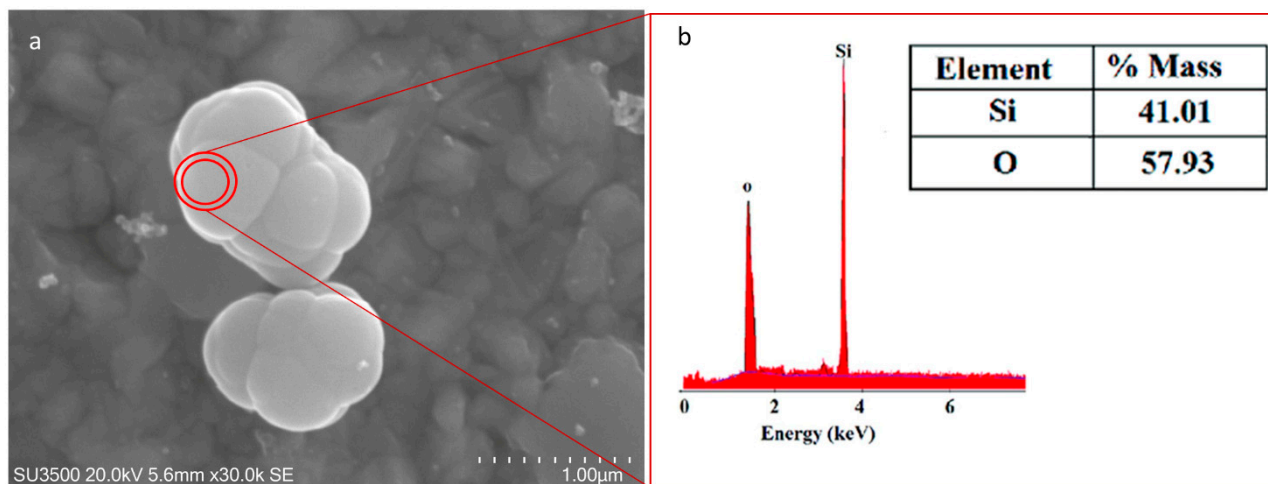


Figure S4. SEM and EDX analysis of SiO₂ nanoparticles. a) SiO₂ nanoparticles aggregate in oval, morula-like microcrystals. b) EDX analysis of the area encircled in red in a, the elemental composition of the area shows the presence of Si and O elements only.

SEM observations help in understanding the dynamic of the consolidation process as it is illustrated in **Figures S5 a-d**. The basic SiO_2 cell unit is shown in **Figure S5a**, and morula-like aggregates of SiO_2 nanoparticles, forming micrometric crystals with pointed endings, are presented in **Figure S5b**. SiO_2 micrometric crystals, due to their pointed endings, may be able to creep into the smallest and deep fractures of the stone, perfectly fitting into the micro stone spaces. This ability to settle neatly into the cracks makes these particles able to promote further crystal deposition and growth on the stone surface, thus allowing a dynamic restoration process (**Figures S5c** and **S5d**) which results in a more homogeneous stone surface.

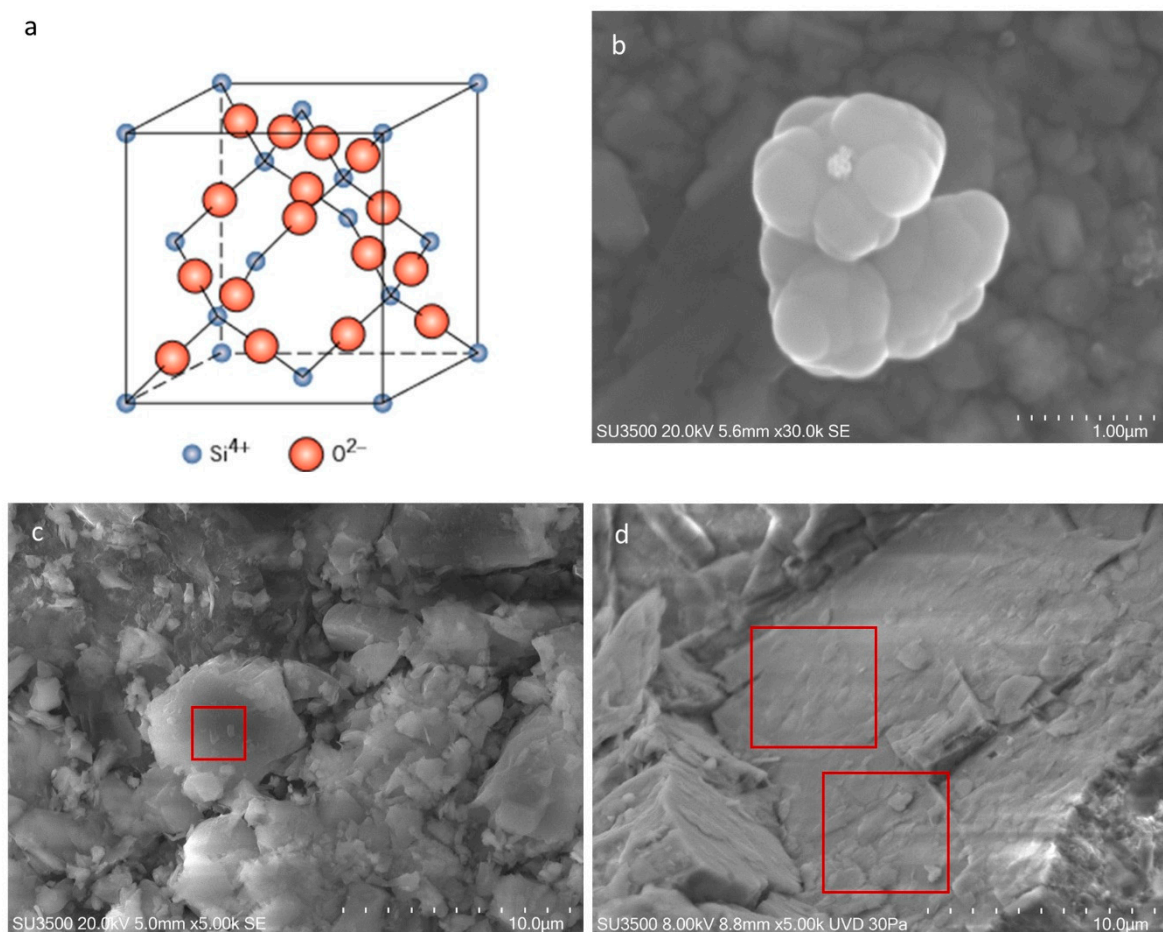


Figure S5. (a) The unit cell of SiO_2 was reproduced in Figure 7 with permission from Dufresne, Ruffledt, and Marshall (2018) by John Wiley and Sons. (b) SEM image of SiO_2 units aggregated in morula-like structures with pointed ends. (c, d) SEM images of the consolidation process. Red squares indicate the SiO_2 nanoparticles fusing with the Pietraforte surface.

In **Figure S6** (A and B), there is an example of the whitening effect due to the treatment of the Pietraforte of the Campanile di San Lorenzo (in Florence) with the dispersion of CaCO_3 nanoparticles, prepared in organic solvent and applied by brush on the Pietraforte surfaces.



Figure S6. Pietraforte surfaces (A and B, respectively, located in two different areas of the San Lorenzo's bill in Florence town) appears completely affected by whitening effect after the consolidation treatment, carried out by applying a suspension of CaCO_3 nanoparticles, prepared in organic working medium, as 1,4-butanediol.

In **Table S2.**, the Viscosity values for different consolidating agents applied on Pietraforte surfaces and prepared in different working medium have also been reported.

From these experimental data, it can be seen that the best analytical performances in terms of lower impediment to the diffusion of the consolidating agent (which is therefore associated with a lower viscosity value for the working medium used to prepare the nanodispersion) are observed for SiO_2 nanoparticles manufactured at the University of Rome Tor Vergata and very well dispersed in aqueous working medium only (as distilled water).

Table. S2. Viscosity values for different consolidating agent applied on Pietraforte and prepared in different working medium.

Nanoparticles	Working medium	Viscosity, [mPa. s]	Temperatures, [°C]	References
Estel1000	white spirit D40	100	R. T.	https://www.ctseurope.com/it/249-estel-1000
SiO_2 nanoparticles	iso-propanol	not relevant	R. T.	[Cao, 2021] in the manuscript
SiO_2 nanoparticles	white spirit D40	not relevant	R. T.	[Pinna, 2018] in the manuscript
PMMA/ SiO_2 / ZrO_2	Augeo/MEK 50/50	1.32	20	[Bergamonti, 2018] in the manuscript

Table. S3. Dimensions and Diffusion features of Thiolated and PEGylated Nanoparticles (compared with those exhibited by the control, as SiO₂ nanoparticles without functionalization, synthesized in this work)

Nanoparticles	Nanoparticle size, nm (DLS)	Medium	Medium viscosity (cP)	Diffusion coefficient x 10 ⁴ nm ² /s (Stokes–Einstein equation)	Diffusion coefficient x 10 ⁴ nm ² /s (Nano Sight)	References
SiO ₂	20 ± 1	water	0.81	1190	998 ± 12	This work
Thiolated	44 ± 2	water	0.89	1115	731 ± 40	[1]
Thiolated	44 ± 2	HEC	5.10	195	593 ± 55	[1]
Thiolated	44 ± 2	PAA	5.10	195	461 ± 28	[1]
Thiolated	44 ± 2	PVP	5.10	195	238 ± 30	[1]
Thiolated	44 ± 2	PEO	5.10	195	172 ± 44	[1]
PEGylated (750 Da)	52 ± 1	water	0.89	943	906 ± 89	[1]
PEGylated (750 Da)	52 ± 1	HEC	5.10	165	614 ± 51	[1]
PEGylated (750 Da)	52 ± 1	PAA	5.10	165	553 ± 23	[1]
PEGylated (750 Da)	52 ± 1	PVP	5.10	165	626 ± 46	[1]
PEGylated (750 Da)	52 ± 1	PEO	5.10	165	721 ± 45	[1]
PEGylated (5000 Da)	68 ± 2	water	0.89	721	834 ± 29	[1]
PEGylated (5000 Da)	68 ± 2	HEC	5.10	126	534 ± 21	[1]
PEGylated (5000 Da)	68 ± 2	PAA	5.10	126	487 ± 6	[1]
PEGylated (5000 Da)	68 ± 2	PVP	5.10	126	547 ± 21	[1]
PEGylated (5000 Da)	68 ± 2	PEO	5.10	126	614 ± 27	[1]
Nano Silica	EtOH: H ₂ O 75:25 (v/v)	1.20 (EtOH): 1.00 (H ₂ O)	20	[Stucchi, 2019] in the manuscript		
SiO ₂ Nanoparticles	H ₂ O	1.00	R.T.	This work		

[1]. Mun, E. A.; Hannell, C.; Rogers, S. E.; Hole, P.; Williams, A. C.; Vitaliy V. Khutoryanskiy. On the Role of Specific Interactions in the Diffusion of Nanoparticles in Aqueous Polymer Solutions. *Langmuir*, 2014, 30, 308–317, doi.org/10.1021/la4029035

In **Table S.3.**, it is clear that the diffusion coefficient of SiO₂ nanoparticles greatly depends on the degree and type of functionalization of the particles themselves. In particular, when the values of the functionalization degree and the viscosity of the working medium result so high, their corresponding diffusion coefficients result lower, if compared with those exhibited by the non-functionalized SiO₂ nanoparticles (like those synthesized, characterized and applied in this work, respectively).

In the following section, the experimental section concerning the viscosimetry measurements and the diffusion coefficient evaluation/quantification have also been reported.

Experimental section

Viscometry.

The viscosity of SiO₂ nanoparticles in aqueous solutions (as working medium) prepared at the optimized concentration of 0.01 mg/mL was measured using a Brookfield DV-II+Pro viscometer (Brookfield Engineering Laboratories, Inc, USA) at 25 °C with an S62 spindle (LV series) at 60 rpm. The SiO₂ aqueous nanodispersions were prepared at five different concentrations (0.01, 0.05, 0.1, 0.5, and 1 mg/mL) in deionized water. Twenty milliliters of each nanodispersion prepared in deionized water (as working medium) were placed into the capillary viscometer and allowed to reach temperature equilibrium for 5 min. The flow time of each sample was measured five consecutive times, and the mean viscosity \pm SD was quantified for SiO₂ aqueous nanodispersion and the aqueous working medium. The relative viscosity was calculated according to the reference [1].

Diffusion Coefficient Measurements.

The diffusion coefficients of nanoparticles were measured using a NanoSight LM10HSGF system. The system was equipped with a scientific CMOS camera and a 532 nm laser with temperature control. NTA 2.3 analytical software was used to capture and analyze three 60 s videos from each sample; the camera level was set to 16, and the temperature was set to 25 °C throughout. All samples were diluted with the aqueous solutions prior to analysis to give 4×10^{-5} mg/mL nanoparticle dispersions (starting from the 0.01 mg/mL as the optimized concentration of the corresponding aqueous SiO₂ nanodispersion). For analysis, a multiple detection threshold, automatic blur, automatic minimum track length, and automatic minimum expected particle size were used, according to the manufacturer's recommendations.