SILICA NANOPARTICLES WITH ANISOTROPIC SHAPE AS FILLERS FOR DENTAL COMPOSITE MATERIALS

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Abstract
Silica nanoparticles with different morphologies were synthesized via the sol gel route by using surfactants as structure directing agents. SEM and nitrogen sorption measurements were applied for characterization. The particles were functionalized and incorporated into a photo-polymerizable matrix to generate the composite material. The mesoporous pore system of the particles could be used as a drug delivery system for silver nanoparticles. The antibacterial properties of silver nanoparticles against E. coli and S. aureus have been investigated as a reference system.

1 Introduction
1.1 Anisotropic morphology of silica nanoparticles
The increased need of esthetic dental materials which are also biocompatible and exhibit good mechanical properties made dental composites to the material of choice. Restorative dental composite materials contain inorganic fillers incorporated into photo-polymerizable organic resins. The monomer of 2,20-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) and the diluents monomer of tri(ethylene glycol) dimethacrylate (TEGDMA) are frequently used dental base monomers. Common fillers are glass splinters, ceramics or nanoscale silica particles which are spherical in shape.[1] Naturally occurring anisotropic crystalline silicate as fillers indicate enhanced mechanical properties due to the anisotropic shape, but may not be biocompatible because of its asbestos-like structure.[2] By using amorphous anisotropic silica particles the mechanical properties of the composite material, e.g. hardness, flexural strength, and wear resistance should be enhanced due to entanglement and bridging effects.[3] However, amorphous silica nanoparticles are biocompatible and approved by the FDA as generally recognized as safe.
The surface of silica particles is covered with hydrophilic silanol groups. This leads to repulsive interactions between the inorganic fillers and the hydrophobic monomers of the resin. As a result the degree of dispersion of the silica particles within the organic matrix is decreased and agglomerates are formed. This leads to decreased mechanical properties of the composite material. To prevent this negative effect surface functionalization of the silica fillers with organic methacrylate groups is applied to decrease the repulsive interactions and

to generate covalent bonds between the inorganic particles and the organic polymer during the photo-polymerization progress.

1.2 Pore system of silica nanoparticles

Commercially available silica filling materials are spherical in shape and manufactured by flame pyrolysis. Therefore these silica particles are nonporous. Anisotropic particles are synthesized via the sol-gel route by using different surfactants as structure directing agents. After the removal of the organic templates by calcination at high temperatures the silica particles exhibit a hexagonal ordered pore system. These pores could be used to build up a local drug delivery system. Different organic or inorganic antimicrobial agents could be incorporated into these pores and provide the composite with antibacterial properties. For this purpose silver nanoparticles were supposed to be generated within the mesoporous system. Silver nanoparticles are known to be nontoxic and safe antibacterial agents for the human body[4]. As a reference system silver nanoparticles within a polyvinylpyrrolidone matrix were tested *in vitro* for antibacterial properties.

2 Results

By the variation of the synthesis parameters various morphologies were obtained, e.g. spheres, fibers, spirals or platelets. The shape and size of the particles were determined by SEM, shown in Figure 1.

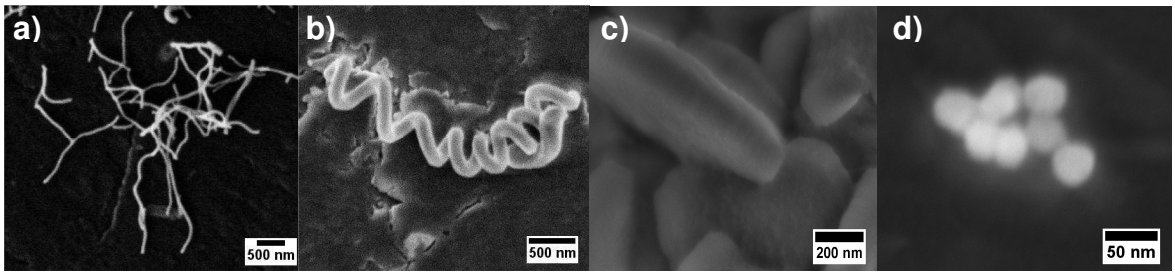

Figure 1. SEM images of silica particles with different morphologies: a) fibers, b) spirals, c) platelets, d) spheres.

The fiber-like silica particles show a very high aspect ratio so they were the first particles incorporated into the polymer matrix of the dental composite materials. The X-ray diffraction pattern of the fiber-like silica particles shows the characteristic reflections of a hexagonally ordered pore system (Figure 2, left). Nitrogen sorption measurements at 77 K were performed to investigate further pore properties. The Brunauer-Emmer-Teller (BET) model was used to determine a specific surface area of 1200 m^2 g^{-1}. The pore size distribution (Figure 2, right) was calculated by using the method of Barrett, Joyner, and Halenda (BJH).

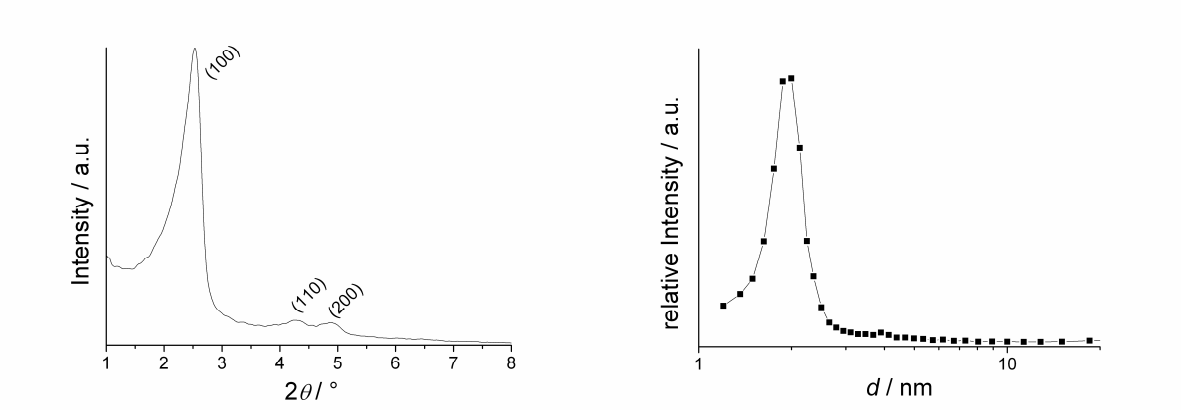

Figure 2. X-ray diffraction pattern (left) and BJH pore size distribution (right) of fiber-like silica nanoparticles.

The average pore size of 2 nm ranges in the transition region between micropores and mesopores. The total pore volume was calculated to be 0.67 cm^3 g^{-1}. Functionalization of the silica surface particles with organic methacrylate groups was applied to improve the interactions between the fillers and the polymer matrix. Figure 3 shows the infra red (IR) spectra of functionalized (top) and unfunctionalized (bottom) silica nanoparticles.

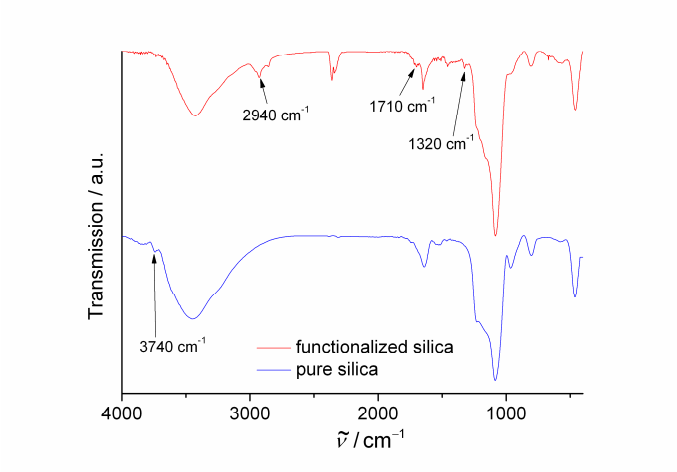

Figure 3. Infra red spectra of functionalized and unfunctionalized fiber-like silica nanoparticles.

The pure silica shows a peak at 3740 cm^{-1} which can be attributed to the Si–OH stretching vibration of free silanol groups at the silica surface. After the functionalization this peak disappears. The appearance of additional peaks indicates the presence of organic groups. These peaks can be assigned to the C–H stretching vibration (2940 cm^{-1}, 1710 cm^{-1}) and the C–O rocking vibration (1320 cm^{-1}). The IR spectra indicate a successful functionalization. The antimicrobial properties of silver nanoparticles were investigated by using a live/dead cell viability assay. The silver nanoparticle-PVP composite (Ag-PVP) shows good antibacterial activity against *Escherichia coli* and *Staphyloccus aureus* (Figure 4). The viability rate of the bacteria decreases significantly at concentrations of 6 µg mL^{-1} (*E. coli*) and 25 µg mL^{-1} (*S. aureus*) respectively.

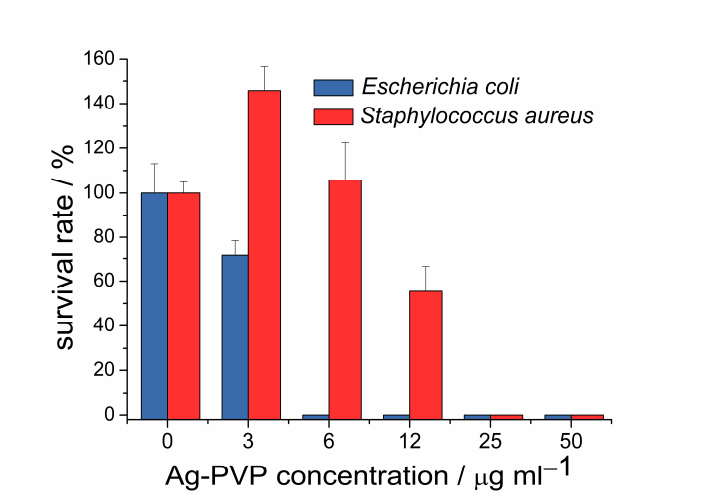

Figure 4. Live/dead cell viability assay of a silver nanoparticle – PVP composite.

Hence, silver nanoparticles are supposed to be promising antimicrobial agents for dental applications.

4 Outlook

The silica nanoparticles with fiber-, platelet- and sphere-morphology were incorporated into an polymer matrix to produce the composite material. The characterization of the mechanical properties has been carried out with three-point flexural tests, Vicker's hardness and ACTA-abrasion[6] tests. Furthermore the effect of shape and surface functionalization needs to be investigated. The testing of the cytotoxicity and the antimicrobial properties of silver nanoparticles within the silica pores are in progress.

5 Materials and testing methods

All chemicals used used as received without any further purification and were obtained from Sigma-Aldrich. Fiber-like silica nanoparticles were prepared by heating a solution of 1.00 g cetyltriammonium bromide (CTAB), 4.50 mL 2 M sodium hydroxide solution in 500 mL deionized water to 60 °C. 6.77 mL tetraethoylsilane (TEOS) and 0.57 mL 3-mercaptopropyl trimethoxysilane (MPTS) were added simultaneously and the solution was stirred for 2 h. The white precipitate was filtered with a frit, washed with water and ethanol and dried at 60 °C. The template was removed by calcination at 550 °C for 5 h after a heating rate of 1 °C min^{-1}.
Spiral-like silica particles were prepared similarly but with a CTAB amount of 2.60 g.
Silica particles with platelet-like morphology were prepared by hydrolyzing 4.48 g Pluronic P-123 triblock copolymer in a solution of 29.80 ml concentrated HCl, 0.73 g $ZrOCl_2 \cdot 8H_2O$ and 150 mL deionized water. The solution was heated to 35 °C, 10.00 mL TEOS were added and stirred for 24 h. The white precipitate was filtered with a frit, washed with water and ethanol, dried at 60 °C and calcination at 550 °C for 5 h after a heating rate of 1 °C min^{-1}.
Spherical porous silica nanoparticles were prepared by dissolving 3.16 g CTAB and 0.23 g diethanol amine in a solution of 75.00 mL deionized water and 13.40 mL ethanol. The mixture was heated to 40 °C, 8.56 mL TEOS were added and stirred for 2 h. The particles were washed by centrifugation at 18000 rpm for 45 min in water and then in ethanol and dried at 60 °C.

Silver nanoparticles within the silica pores were obtained by stirring 100 µg silica in a 0.5 M $AgNO_3$ solution for 7 days. The soaked particles were collected by centrifugation at 6000 rpm for 20 min and calcined at 550 °C for 5 h after a heating rate of 1 °C min^{-1}.
Functionalization of the particles with methacrylate groups were performed by heating a dispersion of 100 µg silica in 4.00 mL toluene, 15.00 µL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 26.00 µL 3-methacyloxypropyl trimethoxysilane to 80 °C under reflux conditions for 2 h. The particles were filtered with a frit, washed with ethanol and dried at 60 °C.
The silver nanoparticle-PVP composite was prepared by dissolving 50.00 mg $AgNO_3$ in a solution containing 50.00 µL H_2O and 30.00 mL acetone. 1.50 g polyvinylpyrrolidone were added and the mixture was stirred for 30 min. The brown precipitate was collected by decantation.

6 References

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