

Tailoring the Surface Chemistry of Nanoparticles in Ceramic Processing

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ABSTRACT

The increasing use of ceramic nanoparticles for the fabrication of novel functional parts and devices has brought several new possibilities and challenges in the field of ceramics. Surface chemistry is known to play a major role during the wet processing of colloidal nanoparticles. In this article, we report two examples where the surface chemistry of ceramic nanoparticles has been tailored to (a) prepare concentrated suspensions for the fabrication of dense films via conventional powder processing and (b) develop bulk macroporous ceramic components from particle-stabilized foams.

1. INTRODUCTION

The use of nanoparticles in ceramic processing has opened up many possibilities for the preparation of ceramic materials with novel and unusual properties.

Nanoparticles allow for a significant decrease in the temperature required to densify ceramic powder compacts. This is of major importance for the fabrication of low-cost solid oxide fuel cells (SOFC). However, the use of nanopowders in well-established processing technologies used for SOFC fabrication has been hindered by the difficulties to prepare suspensions containing high concentrations of nanoparticles. Suspensions with high solids content are crucial for the manufacture of dense ceramic electrolytes via low-cost processing methods such as tape-casting and screen-printing. Concentrated suspensions are also needed for the production of near-net-shape components and in ink-jet technology. In the first example described in this article, we designed new organic molecules to enable the preparation of suspensions with high volume fraction of nanoparticles.

Ceramic nanoparticles have also been recently exploited to produce ultra-stable wet foams that can be further processed into macroporous ceramics with tailored microstructures¹. Macroporous ceramics has been applied for the filtration of molten metals, high-temperature thermal insulation, support for catalytic reactions, filtration of particulates from diesel engine exhaust gases and filtration of hot corrosive gases in various industrial processes². In the second example described here, we tailored the surface chemistry of nanoparticles in order to apply them as wet foam stabilizers for the production of macroporous ceramics.

2. MATERIALS & METHODS

2.1 Processing of concentrated nanoparticle suspensions

Spherical δ -Al₂O₃ particles with an average size of 65 nm and a specific surface area (BET) of 38 m²/g (Nanophase Technologies Co., Romeoville, IL, U.S.A.) were used as model nanoparticles in this work. In order to deliberately vary the adlayer thickness (δ) around the alumina particles, the series of alkyl gallates of different chain lengths ($3 < n < 18$) shown in Fig. 1(a) was used as dispersants. The tri-hydrobenzene group of these molecules exhibit strong affinity to alumina surfaces, while the attached hydrocarbon chain of various lengths allowed us to deliberately change the adlayer thickness around the nanoparticles. Methyl ethyl ketone (MEK, > 99%, Fluka, Buchs, Switzerland) and toluene (99.7%, Fluka, Buchs, Switzerland) were used in different ratios as suspension liquid media. The nanoparticle suspensions were prepared by adding the alumina powder, the dispersant and the solvent into an alumina milling jar, followed by the deagglomeration of the powder for 5 minutes in a planetary mill (300 Hz, PM 100, Retsch GmbH, Haan, Germany). The adsorption of the alkyl gallate molecules on the alumina particle surface was measured by thermogravimetric analysis (STA 449C, Netzsch GmbH, Selb, Germany) of supernatant solutions obtained after centrifugation (5417R, Eppendorf, Hamburg, Germany) of 10 vol% suspensions containing different initial dispersant concentrations. The rheological behavior of the suspensions was evaluated using a cone-plate configuration in a stress-controlled rheometer (Model CS-50, Bohlin Instruments, Cirencester, U.K.).

2.2 Fabrication of macroporous ceramics

Colloidal particles with average diameter of 30, 70 and 200 nm (Nanophase Technologies Co., Romeoville, IL, USA and Sasol North America Inc., Tucson, AZ, USA) were used for the preparation of particle-stabilized foams. Colloidal suspensions were first prepared by adding the dry powders into water upon steady mixing. The suspension solids concentration varied between 15 and 45 vol%, depending on the powder. The nanoparticles were coated by amphiphile short molecules in order to tailor their surface hydrophobicity to different extents. Upon surface hydrophobization, the nanoparticles could be used as stabilizers of air bubbles incorporated into the initial suspension. Foams were produced by thoroughly mixing the concentrated suspensions with a planetary mixer (Major Classic, Kenwood Ltd, Havant, UK) for 3 minutes at full

speed. Fluorescent silica particles and hexyl amine were used to confirm the adsorption of surface modified particles at the air-water interface by confocal laser scanning microscopy. The wet foams were dried in air (1 day) and sintered at 1575°C (2 hours) in order to obtain bulk macroporous ceramics.

3. RESULTS AND DISCUSSION

3.1 Processing of concentrated nanoparticle suspensions

Suspensions containing nanoparticles are usually limited in solids content due to the high relative volume of the dispersant adlayer (Fig. 1(a)) with respect to the particle³. Since the maximum packing density in a suspension is limited to about 63 vol%, the volume of solids is reduced by the considerable volume of the dispersant layer. Therefore, a decrease in the adlayer thickness is required to increase the volume fraction of solids. On the other hand, a minimum adlayer is needed to provide steric repulsion against particle agglomeration due to van der Waals attractive forces. Extensive agglomeration decreases the volume fraction of solids, by reducing the suspension maximum packing density. Thus, there should be an optimum adlayer thickness for which the solids content of nanoparticle suspensions is maximized. In order to determine this optimum condition, the adlayer thickness was deliberately changed using alkyl gallate molecules of various chain length.

The adsorption of alkyl gallate molecules on the surface of alumina nanoparticles is illustrated in Fig. 1(b), using octyl gallate ($n = 8$) as an example. A maximum adsorbed amount of approximately $1.8 \mu\text{mol}/\text{m}^2$ is reached for initial gallate concentrations higher than $3 \mu\text{mol}/\text{m}^2$. All the other alkyl gallate molecules ($n = 3, 4, 12$ and 18) displayed similar adsorption behavior. Therefore, an initial dispersant concentration of $3.3 \mu\text{mol}/\text{m}^2$ was used in all the suspensions subsequently investigated in this study.

In order to favor a stretched conformation of the dispersant molecules adsorbed on the alumina surface, the polarity of the suspension solvent was adjusted for each of the evaluated alkyl gallate molecules. Molecules with longer hydrocarbon chain length ($n > 8$) are more apolar and, therefore, required apolar solvents such as toluene to acquire a stretched conformation on the surface. On the other hand, molecules exhibiting shorter hydrocarbon tail length ($n = 3$ and 4) are slightly more polar and thus needed more polar solvent mixtures to protrude from the surface (in this case a mixture of 65 wt% MEK and 35 wt% toluene).

The dispersant chain length had a remarkable effect on the viscosity of the evaluated suspensions, as shown in Fig. 1(c). A substantial decrease in viscosity was observed by increasing the dispersant tail length. This indicates that the adlayer provided by the dispersants is not sufficiently thick to avoid particle coagulation by van der Waals forces.

For thicker dispersant adlayers, particles are expected to be completely dispersed and to behave as hard spheres in the suspension. Based on this consideration, the optimum

adlayer thickness was estimated by extrapolating the rheological data from Fig 1(c) and calculating the viscosity expected for suspensions dispersed with longer molecules using the Krieger-Dougherty model for non-attractive hard spheres. The results shown in Fig. 2 suggest that an optimum adlayer thickness of approximately 5 nm is required to maximize the solids content of suspensions containing 65-nm alumina particles. Relatively fluid suspensions ($\eta_r < 10^3$) with solids fraction up to 40 vol% are expected by using dispersants that lead to such adlayer thickness around particles.

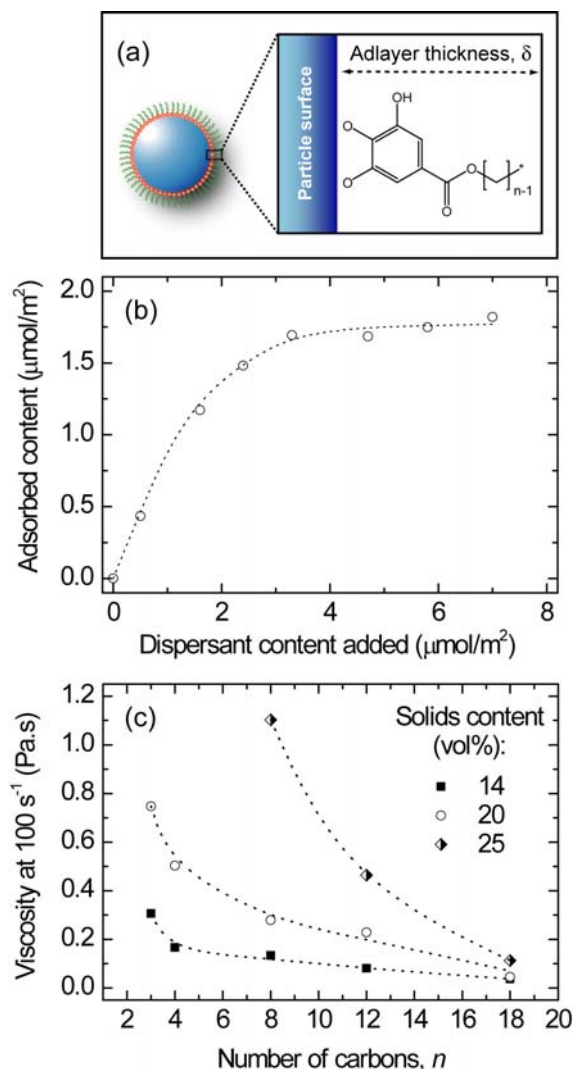


Fig. 1: (a) Illustration of the adsorption of tailored dispersant molecules on the nanoparticle surface. Graph (b) depicts the adsorption of octyl gallate ($n = 8$) on Al_2O_3 nanoparticles dispersed in toluene. Graph (c) shows the effect of the dispersant tail length on the viscosity of alumina suspensions at various solids content.

Based on these results, we synthesized new gallate molecules with tail length closer to the optimum adlayer thickness depicted in Fig. 2. In this case, a polyethylene glycol (PEG) segment was attached to the gallate anchoring group in order to enable the dispersion of nanoparticles in

water. This allowed us to obtain surface charges at low pHs and thus add an electrosteric layer around the particles, which was tuned using different salt concentrations in the suspension to achieve the optimum adlayer thickness.

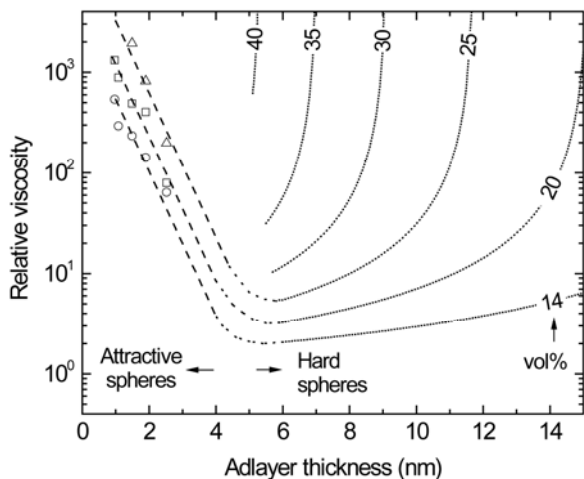


Fig. 2: Effect of the dispersant adlayer thickness on the relative viscosity (η_r) of suspensions containing different solid volume fractions. Symbols refer to measured data (Fig. 1) and dotted lines were estimated from Krieger-Dougherty model for hard spheres³.

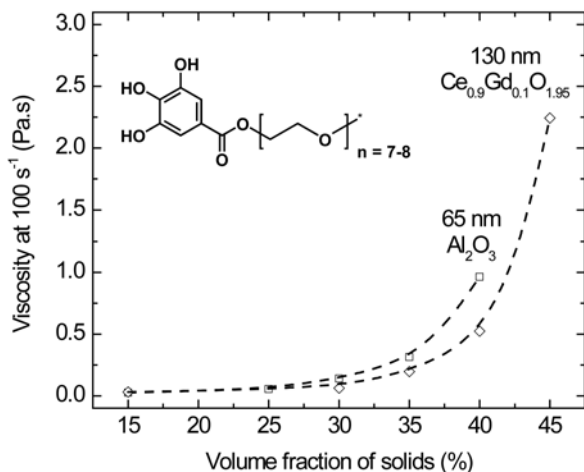


Fig. 3: Viscosity of Al_2O_3 and CGO nanoparticle suspensions (pH 5 and 8, respectively) dispersed with PEG-Gallate molecules (inset) as a function of the volume fraction of solids.

Fig. 3 shows that the resulting PEG-Gallate molecules could indeed provide the optimum adlayer thickness required for high solids content. A solid volume fraction of 40 vol% was achieved using the alumina nanoparticles, as predicted from Fig. 2. The same dispersant was also shown to be suitable for the preparation of doped ceria (CGO) suspensions with high solids fraction (Fig. 3). These suspensions are currently being applied for the production of dense ceria electrolytes for SOFCs.

3.2 Fabrication of macroporous ceramics

In order to produce macroporous ceramics, wet foams were first stabilized through the attachment of colloidal particles at the surface of air bubbles. The attachment of colloidal particles at the air-water interface (Fig. 4(a)) was promoted by deliberately changing the wettability of the particle upon adsorption of short-chain amphiphilic molecules on the surface. Amphiphiles initially added to the suspension render the particle partially hydrophobic by adsorbing with its polar anchoring group on the surface and leaving a short hydrophobic tail in contact with the aqueous phase. Short-chain fatty acids, alkyl gallates and alkyl amines with up to 6 carbons in the hydrocarbon tail were used for that purpose⁴.

A minimum amphiphile concentration was required to impart enough hydrophobicity on the particle surface and induce their attachment at the air-water interface. Above this critical condition, the particles are able to promptly attach to air bubbles incorporated into the suspension. Particle adsorption at an air-water interface after surface modification was confirmed by confocal laser scanning microscopy (Fig. 4(b)).

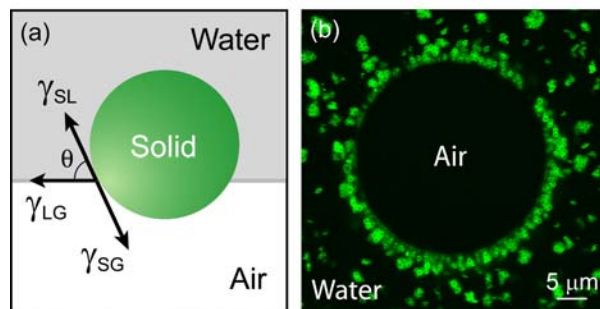


Fig. 4: Adsorption of partially hydrophobic particles at air-water interfaces: (a) scheme of the interfacial tension balance at equilibrium, (b) confocal laser scanning microscopic image of modified silica particles adsorbed around an air bubble.

After the surface modification of particles, air can be easily incorporated by mechanical frothing, injection of gas stream, or initiation of a chemical reaction that releases gaseous by-products directly into the initially fluid suspension. The high diffusion coefficient of nanoparticles in liquids was observed to play a major role on this foaming process, by favoring the ready stabilization of air bubbles incorporated in the suspension. The minimum concentration of particles required for foaming was lowered from 15 to 5 vol% by reducing the particle size from 200 to 30 nm. After air incorporation, the partially hydrophobic particles form a slightly coagulated network throughout the aqueous continuous phase, leading to relatively stiff viscoelastic foams with unprecedented long-term stability.

The stability of particle-stabilized foams prepared with this method is compared in Fig. 5 with that of a surfactant-stabilized shaving foam known to be extremely resistant against coalescence and Ostwald ripening. The particle-

stabilized foam is completely stable against drainage, coalescence and Ostwald ripening for more than 4 days, as opposed to the approximately four-fold increase in average bubble size observed in the shaving foams after only 4 hours (Fig. 5). The outstanding stability achieved with this new method relies on the irreversible adsorption of colloidal particles at the air-water interface of the gas bubbles^{5, 6}, as opposed to the continuous adsorption-desorption experienced by conventional surfactant molecules⁴. Particles irreversibly adsorbed at the interface sterically impede the coalescence of neighboring bubbles and also form a coating layer that restrict bubble shrinkage and expansion in such a way that Ostwald ripening is strongly hindered.

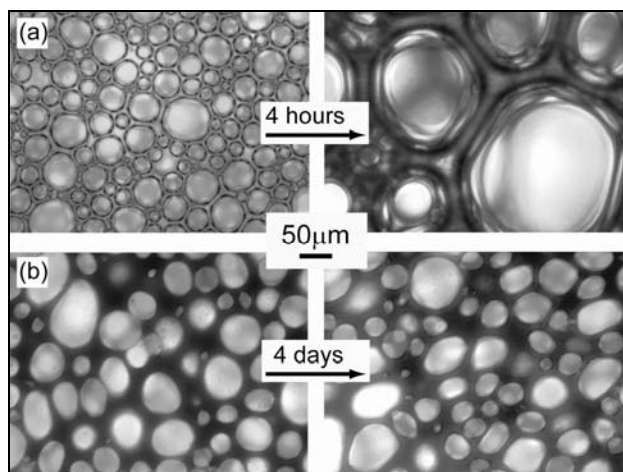


Fig. 5: Outstanding stability of particle-stabilized foams (b) as compared with the coarsening that occurs in a surfactant-stabilized shaving foam (a, Gillette™)¹.

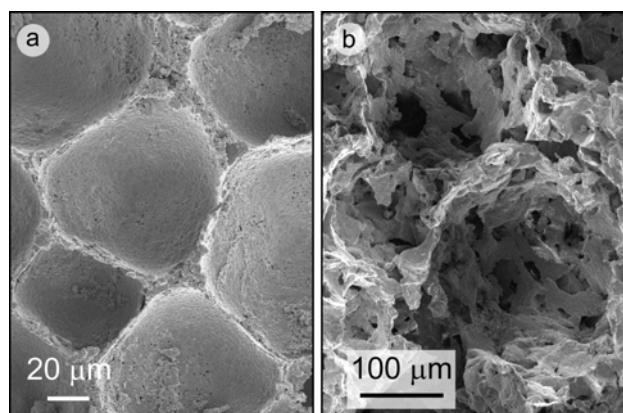


Fig. 6: Open (a) and closed (b) porous microstructures achieved after drying and sintering (1575°C/2h) the particle-stabilized foams.

Due to its remarkable stability, particle-stabilized foams can be directly dried and sintered to obtain macroporous ceramics. This is a major advantage of this novel process in comparison to other methods which require a setting reaction to avoid foam collapse¹. Additionally, the outstanding stability of particle-stabilized foams enables the preparation of highly porous ceramics exhibiting pore sizes

four to five-fold smaller than those achieved with other foaming methods¹. The porosity of foams produced with this method vary typically between 40 and 93%, whereas the average pore sizes can be tuned from approximately 10 to 300 μm. Macroporous ceramics produced from particle-stabilized foams also exhibit a remarkable compressive strength of 16 MPa at porosity levels of 87 – 90% and pore sizes of 30 μm. Porous ceramics with open or closed porosity (Fig. 6) can easily be produced with this simple technique.

4. CONCLUSIONS

Colloidal suspensions with high concentration of nanoparticles were prepared by tailoring the thickness of the dispersant layer on the particle surface. Dispersant molecules with optimal chain length allowed the preparation of suspensions with up to 45 vol% of alumina and doped ceria nanoparticles at reasonably low viscosity (< 1 Pa.s at 100 s⁻¹). Using this approach, nanoparticles can be processed using various well-established ceramic shaping techniques, including screen printing, tape-casting and free-form fabrication technologies.

Tailoring of the surface chemistry of nanoparticles has also allowed us to prepare macroporous ceramics with porosity up to 93%, exhibiting closed or open pores within the range of 10 to 300 μm and remarkable mechanical properties. The outstanding stability of wet foams stabilized by partially hydrophobic nanoparticles allowed for the fabrication of porous ceramics by simple drying and sintering processes. The porous materials obtained by this novel method can be used as filtration membranes, thermal insulators, catalyst supports and scaffold material for tissue engineering and bone replacement.

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