

Chemistry and Technology of Nanoparticles: Preparation, Processing and Application

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ABSTRACT

A fabrication and a processing process of nanoparticles by chemical synthesis routes have been developed for ceramic and nanocomposite materials. The investigation shows that microemulsion and controlled growth processes followed by solvo-thermal treatment can be used for the preparation of agglomerate-free powders to be either incorporated into polymer matrices for nanocomposites or to be processed to ceramics. For obtaining green densities up to 60 % by volume, appropriate surface modification techniques for controlling the particle-to-particle interaction have been developed. As alternative route also leading to nanocomposites, the so-called in situ process has been established. For this route, alkoxide and organic nanomer containing systems are hydrolysed, processed to films or bulk components with optical quality.

1. INTRODUCTION

Besides the manifold investigations of nanostructured materials [1] the preparation of nanoparticles and their use recently have become a very interesting matter of various investigations. Nanostructured materials are defined as materials with mainly crystalline nanoparticles and grain boundary volume fractions of about 50 % and where the properties depend strongly on this grain boundary phase. In opposition to this, nanodispersed systems are considered as systems containing nanoparticles with polymer matrices the physical properties of which are dominated by the nanoparticles. These materials can be defined as polymer matrix nanocomposites and have already shown interesting applications [2, 3, 4]. One of the most important topics for the fabrication of this type of composites is to produce agglomerate-free nanoparticles and to disperse them into a matrix avoiding agglomeration. For this reason the interfacial free energy is a governing factor between the nanoparticle and the matrix has to be controlled. A perfect dispersion can only be maintained if the free energy for agglomeration is on a higher level than the free energy of the dispersion. To achieve this it is necessary to control surface chemistry of the nanoparticle during fabrication and dispersion. In the following a short overview is given how chemical synthesis can be used to achieve these objectives.

2. GENERAL CONSIDERATIONS

Nanoparticles have been known in form of sols or colloidal dispersions for quite a while. In sol-gel chemistry, so-called particulate sols, in general, are composed of dispersed particles with sizes of several nanometers. They can be prepared by so-called sol-gel reactions from alkoxides [5] and, in general, are rather stable at appropriate pH values. The stability is based on the so-called electrostatic stabilization, which takes place by absorption of ions from the solution, mainly protons or hydroxyls. Destabilization of the sols leads to rapid aggregation (gelation). For using these particles out of the conventional sol-gel field, the

gelation step has to be either controlled or to be avoided. „Controlled“ means that the arrangement of the particles while growing together should take place in a controlled manner so that, for example, the density or the number of contacts between the small particles take place or are formed in a desired way. This leads to the question of how to control the surface reactivity of these particles. Avoiding gelation means that interaction of the small particles is controlled in a way that no macroscopic type of aggregation leading to brittle materials takes place. If it is possible to make achievements in this direction, the use of small particles becomes extremely interesting since a large potential is assumed. In fig. 1, a short survey over the basic potential of nanoparticles is given.

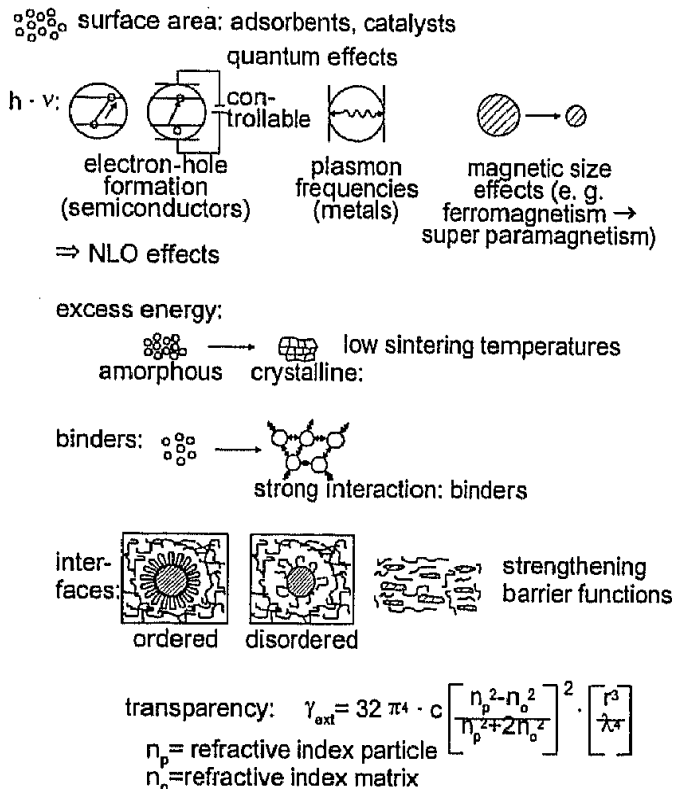


Fig. 1: Examples of the potential of nanoparticulate systems for materials for new material properties.

This overview shows that, depending on the basic property to be considered, interesting properties should be obtainable in materials. For example, if the correlation length of density fluctuations in materials can be kept distinctly below the Rayleigh scattering limit (about 1/20 of the wavelength of light to be used and depending on refractive index differences), optical transparent materials can be produced from a variety of systems, especially if the particles are nicely dispersed in a transparent matrix. In this connection, it has to be mentioned that for dispersing particles in liquid or viscous matrices, the interfacial free energy is the governing parameter. As shown in systematic investigations [6], the dispersion of nanoparticles in polymer melts can only be achieved if the interfacial free energy between the particle surface and the polymer matrix can be reduced to a level below the free energy of aggregation. Interfacial free energy can be calculated from the wetting angle, but is very difficult to measure between a nanoparticle surface and a polymer.

Other interesting features are quantum properties related to the small particle size (electron-hole formation, photovoltaic properties, non-linear optical properties, catalytic properties), change of mechanical properties of matrices if nanoparticles are well dispersed [7], structural effects on the polymer matrix (formation of ordered or disordered interfaces or nucleating effects on the crystallization of polymers), effects resulting from the high surface area (absorption or catalysis), binding properties meaning that interparticulate forces can be used to bind parts together, rheological properties resulting from the particle-to-particle interaction as far as these interactions can be controlled. These few examples show that there is an interesting potential in using nanoparticles for material development and tailoring [8].

As pointed out above, the surface chemistry of the particles seems to play a very important role on physical as well as processing properties of the particles. For this reason, it

is very important to develop methods to influence the surface properties, for example, by molecular surface modification.

3. METHODS FOR PREPARING NANOPARTICLES

Two routes have been developed for the preparation of nanoparticles [8]. One method uses a thermodynamical approach to control nucleation and growth, and the second method is based on microemulsion techniques. In fig. 2a and b the schematics of these processes is shown.

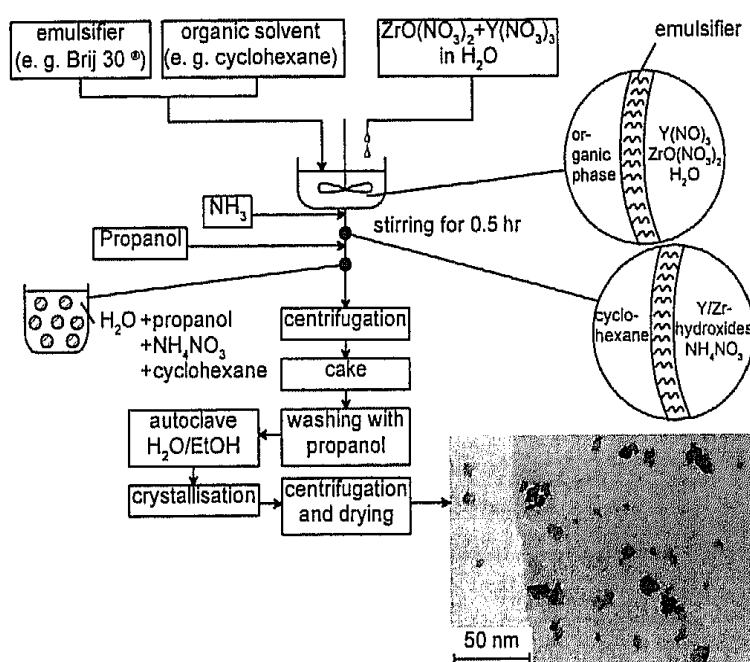


Fig. 2a and 2 b: Fabrication of nanocrystalline yttria-reinforced ZrO_2 and SnO_2 by microemulsion and the controlled growth routes.

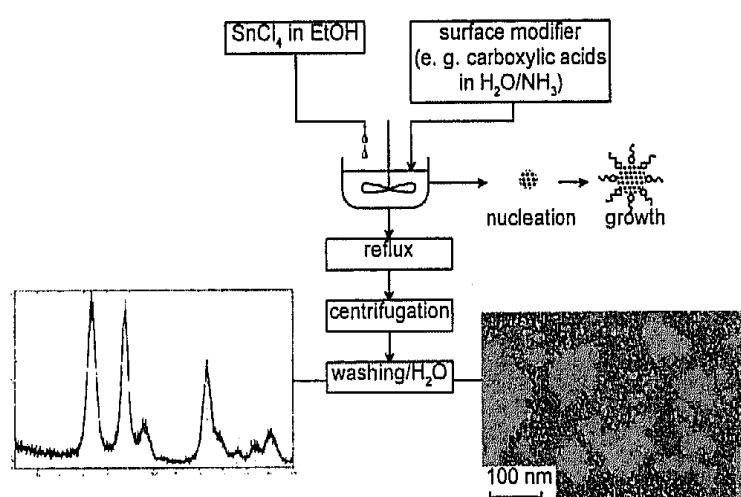


Fig. 2b

As precursors simple salts as well as alkoxides can be used. The microemulsion route has been investigated in detail [9,10]. It was shown that a variety of different systems can be synthesized by microemulsion techniques as well as by the controlled growth process. In the cited literature details

about the synthesis and preparation techniques are given. For obtaining sufficient crystallinity, especially in systems with a high amorphous fraction, a solvo-thermal treatment is necessary. This treatment has to be carried out under so called protective agents which either can be surface charges or surface modifiers sufficiently strongly bonded to the surface [11]. It was shown that by appropriate choice of reaction conditions the nano-particulate properties could

be maintained through the solvo-thermal treatment. Powders obtained from this process are weakly agglomerated and can be completely deagglomerated when dispersed in appropriate liquids depending on the surface modification. If ambivalent molecules, such as proteins, are used for surface modification, the systems can be dispersed easily in water. If molecules are used having a hydrophobic shell, the materials can be dispersed in organic solvents. Meanwhile, the solvo-thermal treatment has been scaled up to a continuous-flow process using linear flow-tube type autoklaves. Meanwhile, up to 5 kg/hour of material can be produced. Microemulsion and controlled growth techniques have been developed for zirconia and yttria-reinforced zirconia [12 - 16].

4. PROCESSING OF NANOPARTICLES

Processing of nanoparticles to ceramics and nanocomposites using nanoparticles can be carried out through two basically different routes. The incorporation of nanoparticles into polymers to form nanocomposites can be carried out either by the incorporation of nanoparticles produced independently of the matrix system or by nanoparticles in situ formed within the matrix system. The formation of nanoparticles within the matrix system has been described in ref. [17]., where zirconia particles of about two nanometers in diameter are formed from zirconia alkoxides during hydrolysis and condensation in a methacrylate-containing matrix. In figure 3 these both routes are described schematically.

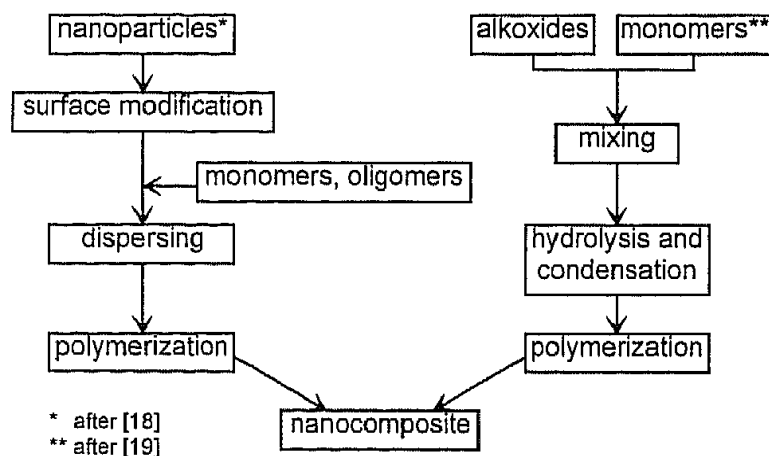


Figure 3. Schematics of the separate and in situ preparation routes of nanocomposites.

Whereas in the in situ route the phase separation takes place by a nucleation and growth process and the particle size is mainly defined by the nucleation frequency, the separate route requires an adaption of the particle surface to the matrix in order to keep the interfacial free energy low enough. As an example, SiO_2 filled epoxy/MMA-based polymers have been prepared with colloidal silica which is commercially available (Levatis[®], Bayer company) which was surface-modified by a tetrahexylammonium hydroxide which is able to make the SiO_2 surface hydrophobic enough to get the particles dispersed in the monomeric matrix to an optical clear and transparent system. By addition of UV-initiators, this system can be photocured at room temperatures even with 30 % of volume of SiO_2 nanoparticles to highly transparent composites. Due to the perfect dispersion of the nanoparticles the viscosity of the system is hardly affected. The same concentration of uncoated SiO_2 (e.g. fumed silica)

leads to brittle gels. This system is used for optical glass fibre to chip coupling and presently introduced into the market [18].

In situ prepared zirconia nanocomposites as described above with two nanometer zirconia particles have been investigated by electron diffraction measurements and show that the zirconia is crystallized in monoclinic even if the processing temperatures never have exceeded 120 °C. In a viscous state, the zirconia nanoparticles still carry electric charges which can be used for electrophoretic gradient formation [19]. It has been shown that by employing electric fields to a viscous rod of 1 cm in diameter the zirconia particles can be upconcentrated and the resulting refractive index difference of 0,07 was obtained. Disks cut off of these polished rods show the behaviour of optical lenses. These few examples show that if appropriate methods are used for the processing of nanoparticles nanocomposites with interesting properties can be obtained.

Nanoparticles coated with non-reactive short molecules chemically bonded to the surface can be used to reduce the interaction between particles in a way that high-solid content sols or green bodies can be obtained. This was demonstrated for titanium nitride coated with guanidino propionic acid or boehmite coated with propionic acid [20 - 22]. In these cases, despite the small particle size of 15 nanometers in the case of alumina and 30 nanometers in the case of titanium-nitride green densities could be obtained up to 60 % by volume which is extremely high compared to green bodies prepared by the sol-gel process. In the case of titanium nitride dense sintered bodies could be obtained at temperatures of about 1300 °C only (compared to micrometer-sized green bodies (2200 °C)). Zirconia coated with propionic acid could be sintered to dense green bodies below 1100 °C. The green bodies are translucent and can be plastically formed, for example by extrusion or tape casting. Using this approach, foils could be fabricated with thicknesses down to 3 nm which can be laminated on top of ceramic substrates and sintered to porous membranes or completely densified to dense layers [23, 24].

5. CONCLUSIONS

In the previous examples it could be shown that by using chemical methods it is possible to synthesize nanoparticles efficiently in a well characterized form. These nanoparticles can be used in relatively simple processing techniques either to form composite materials or ceramics. In future investigations it will be necessary to exploit the processing technologies to investigate how far other systems are available through these techniques.

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