Nanostructured materials. Selected Synthesis Methods

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Nanostructured materials. Selected Synthesis Methods*: In this article various ways to make nanocrystals are presented. It is possible to produce a large variety of nanoparticles, semiconductors, metals, oxides and alloys, by using colloidal self-assemblies as nanoreactors. The limitations in using these colloidal solutions to produce nanomaterials are pointed out. Synthesis and assembly strategies accommodate precursors from liquid, solid, or gas phase; employ chemical or physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate nanostructure building blocks within the final material structure..*

***Key words:** Nanotechnology, Nanoparticles, Synthesis Methods*

INTRODUCTION

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential to impact both the ways by which materials and products are created and the range and nature of end product functionalities. It is already having significant influence on the markets which is expected to strengthen in the future.

During the last decade, due to the emergence of a new generation of high technology materials, the number of research groups involved in nanomaterials has increased exponentially [1,2]. Nanomaterials are implemented in various industries, e.g. chemistry, electronics, high density magnetic recording media, sensors and biotechnology. This is partly due to their novel properties differing from both the isolated atoms and the bulk phase. An ultimate challenge in the research of these materials now is the creation of perfect nanometer-scale crystallites (by size and shape) which can be replicated in unlimited quantities in a state that might behave as pure macromolecular substances [3]. The choice of method of synthesis of the nanomaterial is crucial for the prediction of their properties and their implementation in different industries. Physical and chemical methods for preparation of nanomaterials were developed: ball milling, gas-phase flame reaction and condensation, chemical reduction and coprecipitation aiming to control the particle size (up to 10 nm) and morphology. More recently, new preparation methods have been developed such as sonochemical reactions, gel-sol, microwave plasma and low energy cluster beam deposition. In 1988, we developed a method based on reverse micelles (water in oil droplets) for preparing nanocrystals [3].

SYNTHESIS AND ASSEMBLY

Synthesis and assembly strategies accommodate precursors from liquid, solid, or gaseous phase, employ chemical or physical deposition approaches and rely on either chemical reactivity or physical compaction to integrate nanostructure building blocks within the final material structure.

Several techniques are used to produce nanomaterials by soft chemistry to obtain either amorphous or crystalline nanoparticles. Whatever the procedure is, the major factors involved in controlling the size or shape of nanoparticles are confinement, electrostatic interactions, reactant solubilities and large local amounts of reactant. After or during the production, nanoparticles have to be passivated to prevent coalescence. One of the first approaches to make nanoparticles was based on the change of the solubility product of reactant with temperature [4]. This controls the particle size. Simultaneously, syntheses of nanoparticles in aqueous solution in presence of a charged polymer that strongly interacts with one of the reactants were developed [5,6]. Data obtained by using colloidal self-assemblies as a nano-reactor to control the nanocrystal sizes are given below.

REVERSE MICELLES

Reverse micelles are water in oil droplets stabilized by surfactant [7]. The water to surfactant concentration ratio, w=[H_2O]/[S] linearly controls the size of the droplet. Reverse micelles are subjected to Brownian motion and during these collisions the droplets combine to form a dimer and this is accompanied by an exchange of their water contents. The dimer dissociates to restore the reverse micelles. These two properties (control of the droplet size and the exchange process) make possible the use of reverse micelles as a nano-reactor. Two micellar solutions are prepared. Each contains one of the reactants. By mixing these solutions, a chemical reaction takes place and nanomaterials are produced [1,2]. The droplet size, which is controlled by w, stipulates the size of the particle. This procedure has been used to obtain a large variety of materials such as semiconductors, metals [1] and oxides.

When the two reactants are present as salts, amorphous nanomaterials are formed. *Vice versa*, when one of the reactants is a functionalized surfactant (the reactant is the counter ion of the surfactant) nanocrystals are produced [7].

Fig.1 shows a model where one of the reactants is functionalized surfactant. On increasing the water content, i.e., the size of the nano-reactor (water in oil droplet), the particle size increases (Fig. 1).

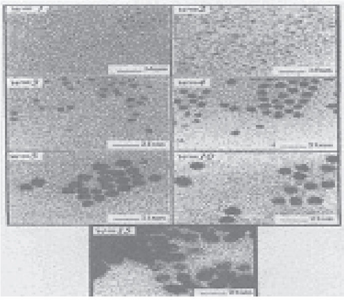

Fig.1: TEM patterns of copper nanocristals obtained in mixed reverse micelles (Na(AOT) – Cu($AOT)_2$) at various water contents A w=2, B w=5, C w=40

NORMAL MICELLES

Normal micelles are oil in water suspension where the length of the surfactant alkyl chain controls the size of the droplets. Most of the nanomaterials produced are made using functionalized surfactants. This induces a significant increase of the local amount of reactants to reach local supersaturation. Conversely to reverse micelles, there are no limitations for the reactants in normal ones. Normal micelles act as a polymer which controls the nanoparticles size. This made it possible to obtain CdS and copper nanocrystals, as well as magnetic fluids. In the latter case, transition metals involved in the ferrofluids form the counter ions of the micelles. This technique makes it possible to produce a large variety of alloys with compositions similar to these of the reactants used for the syntheses. The size of the nanocrystals, which can vary from 2 to 8 nm, is controlled by the micellar concentration [8].

HYDROTHERMAL SYNTHESIS OF NANOMATERIALS

Hydrothermal processing is a non-conventional method to obtain nanocrystalline inorganic materials. A direct precursor-product correlation exists allowing synthesis of almost any material without the presence of further structure directing agents [9,10]. The synthesis method uses the solubility of almost all inorganic substances in water at elevated temperatures and pressures, and subsequent crystallization of the dissolved material from the fluid. As implemented in the name, water plays an essential role in the precursor material transformation at elevated temperatures. According to the phase diagram of water, only the branch between liquid and gaseous states is essential for further considerations: below 100°C the equilibrium vapor pressure of liquid water is below 1bar; above the boiling point the important hydrothermal pressure range is available. Two different operation modes can be distinguished in general.

PRINCIPLES AND OPERATION MODES

Both physical and chemical parameters can be varied systematically during the hydrothermal processing in such a way that a direct precursor-product correlation can be established. However, hydrothermal processing is rather complex because a great number of interacting parameters play essential roles [11,12]. The influences of these parameters are a problem which has not yet been solved well enough. Temperature plays an important role in kinetics of product formation, as well as on the thermodynamic stability of the product phase. Pressure is essential for the solubility, the supersaturation range stipulating the crystallization process and for the thermodynamic stability of the product phase (e.g. a too high synthesis pressure leads to crystallization of denser phases). To avoid the influence of the pressure generating temperature, the external pressure mode is actually preferred since low temperature-high pressure syntheses are only available by this highpressure hydrothermal synthesis (HPHS) mode. Time is also an important parameter because the synthesis of kinetically stable phases are favored in short term processes while the thermodynamically stable phases are generally formed in long term experiments under corresponding temperature-pressure regime. This is due to the increased solubility and recrystallization of the already formed phases. However, some reaction related conditions such as convection within the reaction vessel and the precursor materials state of aggregation (e.g. whether they are present as macroscopic crystals, nanocrystalline phases or glass) should not be neglected in the effort to control the process parameters.

RAPID EXPANSION OF SUPERCRITICAL FLUID SOLUTIONS (RESS)

If water is used in the RESS process as the solvothermal medium, the precursor material is dissolved under high pressure and high temperature conditions. The dissolution process is stopped before spontaneous nucleation occurs.

For practical purposes, this is achieved under dynamic flow conditions. Nucleation without further growth is performed by an abrupt decrease of the solubility by expansion through a heated nozzle into a medium under ambient temperature and pressure conditions, inducing spontaneous nucleation of the dissolved materials without significant crystal growth [13,14,15]. Pressure, temperature and time of exposure to hydrothermal conditions are important parameters in order to obtain the desired nanocystalline materials.

RAPID THERMAL DECOMPOSITION OF PRECURSORS IN SOLUTIONS (RTDS)

The method of rapid thermal decomposition of precursors in solutions (RTDS) is based on high pressure high temperature hydrothermal processing. Here, water is used for hydrothermal reactions of precursor materials already dissolved under environmental conditions, leading to precipitation of a nanocrystalline product. The only brief exposure of a few seconds of the pre-pressurized precursor solution to high temperatures (ca. 300-450°C) initiates particle nucleation but prevents subsequent crystal growth of the nucleated product. In contrast to the standard HPHS conditions, the hydrothermal process is used to conduct reactions in the solution which means that it is performed under dynamic flow and subsequent quenching to ambient pressure and temperature conditions. The precursor material used depends on the material to be synthesized and it has to be, to a certain extent, soluble in water under ambient conditions. Therefore, inorganic salt precursors with moderate to high solubility under ambient conditions are used.

HIGH PRESSURE HYDROTHERMAL SYNTHESIS (HPHS)

High pressure hydrothermal synthesis (HPHS) of nanocrystalline materials has to be controlled by the process parameters temperature, pressure and time, as well as the physical and the chemical parameters of the materials system under investigation.

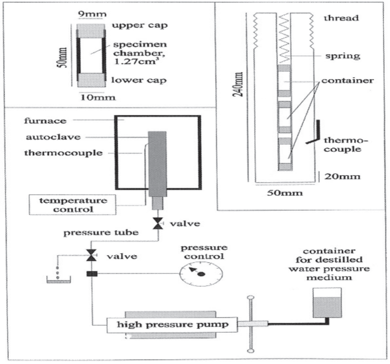

Fig.2: Facilities of standart high pressure hydrothermal synthesis (HPHS)

GLASSY PRECURSOR TRANSFORMATION TO NANOMATERIALS

The high pressure hydrothermal transformation of glassy precursor materials has been successfully employed for systematic synthesis of zeolites under formation conditions close to natural ones [16,17,18]. Here, the vitreous state of aggregation is essential for the successful synthesis because the precursor material solution has composition identical to that of the zeolite product at any time of the experiment. Under these conditions, the zeolite phase formed is thermodynamically more stable than the glassy precursor. Nucleation and subsequent growth will only take place in the range of supersaturated solution. Experiments have shown that homogeneous zeolite nucleation from the supersaturated solution at a chosen hydrothermal pressure 1 kbar is possible in a wide temperature 33 range (at least between 30°C and 400°C) [19]. Further experiments have demonstrated [20], however, that the temperature range of crystal growth is restricted when glasses are used as precursors under standard HPHS conditions. Long term experiments lasting 60 days confirmed that a limited quantity of glass precursor available in the closed container, as well as the high resistance to redissolution of the zeolite product formed enable the synthesis of nanocrystalline materials. At lower temperatures, microscopic crystals were synthesized because the dissolution rate of the glassy precursor is of lower degree of supersaturation, so crystal nuclei grow continuously by consuming the dissolved material at the same rate. Carrying out this experiment at different temperatures, it can be shown that if the dissolution rate becomes too high for a continuous crystal growth repeated nucleation can be observed instead. As can be seen, the maximum crystal size observed at 200°C is about 500nm. Under the same experimental conditions, only nanocrystalline material can be observed at 220°C, too small in size to be resolved by scanning electron microscopy.

Figure 3 shows a SEM micrograph of nanocrystalline Li-Fe-Silicate obtained by 28d PHS at 1 kbar, while at both lower and higher temperatures different microcrystalline materials were synthesized, respectively.

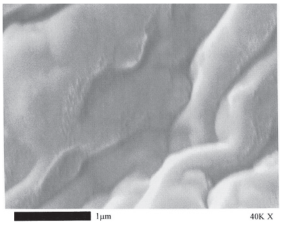

Fig.3: Nanocrystalline Li-Fe-Silicate obtained by HPHS (glass precursor with $Li_2OxFe_2O_3xSiO_2$ composition, 1 kbar water pressure, 200 °C 28d)

CONTROLLED RECRYSTALLIZATION OF NANOMATERIALS

Nanocrystallinity is present if no or only very negligible crystal growth has occured. Some inorganic materials like the class of hexacyanometallates with transition metal ions as structural elements show very low solubility in aqueous solutions under ambient pressures [21].

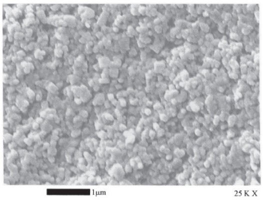

Fig.4: Crystals of re-crystallized nanocrystalline Prussian blue – $KFe^{III}[Fe^{II}(CN)_6]$, obtained by high pressure hydrothermal treatment of a precipitated precursor of the same composition (500bar water pressure, 66^0C, 42d)

SHORT TERM PRECURSOR TRANSFORMATION TO NANO-MATERIALS

Under extreme synthesis conditions, all the initial materials formed underwent dissolution and re-crystallization; that is why the hydrothermally obtained materials are formed under conditions close to equilibrium. To keep the product particle size in the nanometer range, all precursor reaction processes have to occur very rapidly, so that the whole process should be finished within several hours in order to avoid significant growth of the product particles. Various nanocrystalline materials have been obtained in this way.

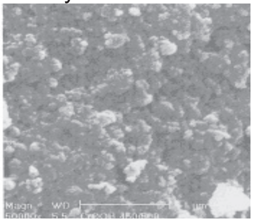

Fig.5: Agglomerated nanocrystals (identified as CrOOH by XRD) obtained by high pressure hydrothermal treatment of coarse grained $Cr(OH)_3$ (500bar water pressure, 390^0C, 6h).

GAS PHASE SYNTHESIS AND SOL-GEL PROCESSING

Major efforts in nanoparticle synthesis can be grouped into two broad areas: gas phase synthesis and sol-gel processing. Nanoparticles with diameters ranging from 1 to 10 nm having consistent crystal structure, surface derivatization, and a high degree of monodispersity have been prepared by both gas-phase and sol-gel techniques. Typical size variances were about 20%; however, for measurable enhancement of the quantum effect, this must be reduced to less than 5% [22]. Initial development of new crystalline materials was based on nanoparticles generated by evaporation and condensation (nucleation and growth) in a subatmospheric inert-gas environment. Various aerosol processing techniques have been reported to improve the production yield of nanoparticles. These include synthesis by combustion flame; plasma; laser ablation; chemical vapor condensation; spray pyrolysis; electrospray; and plasma spray [23].

Sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment. Size distribution of semiconductor, metal and metal oxide nanoparticles can be manipulated by either dopant introduction or heat treatment. Better size and stability control of quantum-confined semiconductor nanoparticles can be achieved through the use of reverse micelles, polymer matrix architecture based on block copolymers or polymer blends, porous glasses, and ex-situ particle-capping techniques[24,25]

SCALEUP

Scaleup production is of great interest for nanoparticle synthesis. High energy ball milling, already a commercial high-volume process, as mentioned above, has been instrumental in generating nanoparticles for the preparation of magnetic, structural, and catalytic materials. However, the process produces polydispersed amorphous powder, which requires subsequent partial recrystallization before the powder is consolidated into nanostructured materials. Although gas-phase synthesis is generally a low production rate process in research laboratories (typically in the range of 100 milligrams per hour), higher rates of production (about 20 grams per hour) have been demonstrated at Ångström Laboratory at Uppsala University in Sweden. Even higher production rates (about 1 kg per hour) are now being achieved commercially. For sol-gel processing, the development of continuous processing techniques based on present knowledge of batch processing has yet to be addressed for economical scaleup production of nanoparticles. Other sol-gel related issues concern the cost of precursors and the recycling of solvent. Overall, sol-gel processing is attractive for commercial scale-up production [26].

CONCLUSIONS

Nanostructure science and technology is clearly a very broad and interdisciplinary area of research and development activity worldwide. It has been growing explosively in the past few years, since the creation of new materials and devices from nanoscale building blocks could access new and improved properties and functionalities. While many aspects of the field existed well before nanostructure science and technology became a definable entity during the past decade, it has really only become a coherent field of endeavor through the confluence of three crucial technological streams: new and improved control of the size and manipulation of nanoscale building blocks; new and improved characterization (e.g., spatial resolution, chemical sensitivity) of materials at the nanoscale; new and improved understanding of the relationships between nanostructere and properties and how these can be engineered.

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