

NOVEL METHOD FOR NANOCRYSTALLINE MATERIALS SYNTHESIS THROUGH AN ULTRAASCOUSTIC ASSISTED HYDROTHERMAL METHOD COMBINED WITH MICROWAVE HEATING

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Abstract: a new hydrothermal method for nanosized particles synthesis, by combining the ultrasonically assisted hydrothermal method with heating in microwave fields is developed. The method cumulates the advantages of classical hydrothermal method, with those of ultrasonically assisted hydrothermal method and microwave assisted hydrothermal method, by eliminating the disadvantages of each separate method.

Keywords: nanocrystals, hydrothermal synthesis, ultrasonic, microwave

1. INTRODUCTION

Nanocrystalline materials, pure or doped, proved to be of great importance and utility in a wide field of applications, due to their very special properties, fundamentally different from the properties of macroscopic materials. The applications could vary from solar energetic, medicine, agriculture, different sensors, to photocatalytical purifiers, etc. Because of extraordinary potential of these materials, a very fast development for nanostructured materials obtaining technologies occurred, and now worldwide keep searching new synthesis methods, with reduced raw materials, energy and time consumptions, by non-polluting ways.

One of the classical nanostructured materials obtaining methods is the hydrothermal method, with temperatures ranging from 100°C to 1000°C and pressures from 1 bar to thousands of bars. The main advantages of the hydrothermal method are:

(a) Pollution is minimized because of the closed system conditions and the reagents can be recycled,

(b) Kinetics of reaction are greatly increased with a small increase in temperature,

(c) Generally single crystals are obtained ,

(d) New metastable products can be formed,

(e) no precipitants are needed in most cases and thus the process is cost-effective,

(f) high purity products can be obtained from impure feedstock. The synthesis take place regularly at lower temperatures than those needed in open atmosphere, and thus the energetic consumption is considerably

reduced.

Although the hydrothermal method is very versatile, one of the main drawbacks is the low kinetics at any given temperature. In order to increase the kinetics of crystallization and to improve the quality of nanocrystals, one can introduce ultrasonic or microwave fields in the hydrothermal system, each of them having some advantages and disadvantages.

The present article refers to a novel method, namely to combine the ultrasonic assisted hydrothermal method with the hydrothermal method in microwave field, in order to have benefits from each of the two ones and to eliminate the disadvantages of each individual method.

Next, we will present the two above mentioned methods, which are usually known as « non-conventional hydrothermal methods », but they tend to become already classical methods in the nanocrystalline materials synthesis.

2. ULTRASONICALLY ASSISTED HYDROTHERMAL METHOD

In the Ultrasonically assisted method, the autoclave containing the growth medium/solution is heated in a classical electrical oven, and the solution is bombarded with ultrasonic waves, either through the autoclave's walls or bottom, either directly, the sonotrode being immersed into the solution. Due to the effects caused by the cavitations in the growing solution (violent implosions of vapor bubbles, micro streams, etc) nanomaterials with low dimensional dispersion are obtained, and most important,

the crystallization duration is dramatically reduced, kinetics improved and the reactions can take place at significant lower temperatures than in classical hydrothermal methods. The reduction in crystallization time is due on one hand to the multiplication of the nucleation centers because of cavitations, but also to the agitation caused by ultrasonic waves that feeds the new-formed crystals with fresh solution, on the other hand. Better (lower) dimensional dispersion is obtained because the growth of the nanocrystals is stimulated only until reaching a critical limit, but also the conglomerates formation is inhibited and the already formed ones are broken by the cavitations. Using ultrasonication in nanocrystals synthesis has, therefore, obvious advantages. The main disadvantage consists in the heating way, which is achieved by classical means, in electrical ovens, with resistive elements.

These ovens have high thermal inertia; heat transmission take place through the autoclave's walls, which is often made by heat insulating materials, such as Teflon. Low speed heating (even if we don't consider the longer time needed for the entire process) has negative effects on the crystallization itself, because long transitory times could lead to premature unwanted crystallizations, at too low temperatures, and therefore to obtaining of nanocrystals with hard controllable characteristics. High thermal inertia has also negative effects when cooling the system, special measures are required to speed up the cooling process and therefore to reduce the total time needed for a synthesis cycle.

3. MICROWAVE ASSISTED HYDROTHERMAL METHOD

As stated in the above, also the microwave-hydrothermal method has distinct advantages over the classical hydrothermal method in the crystallization of different kinds of nanoparticles. The main advantage of microwave introduction in hydrothermal process is extremely rapid kinetics for synthesis. Crystallization times can be reduced up to 10-50 times compared with classical hydrothermal processes. On the other hand, using microwave heating, we achieve very rapidly (tens of seconds-minutes) the working temperature, in the whole mass of the solution. Transitory times

are eliminated, also unwanted low-temperature crystallizations, and the time and energy economies are obvious. Among the method's disadvantages we can say:

(a) The lack of an effective solution agitation, which can lead to some temperature non-uniformities or even some dangerous «hot spots», can occur,

(b) Dimensional uniformity of the obtained nanocrystals can be very low,

(c) Growing nanocrystals tend to settle down on the bottom of the autoclave and to form conglomerates,

(d) Because the geometry of microwaves pattern in non-ideal microwave ovens, usually the temperature significantly varies along the autoclave and because the lack of convection currents, unwanted temperature gradients could appear.

4. THE COMBINED MICROWAVE-ULTRASONIC HYDROTHERMAL METHOD

The present novel method, developed in the National Institute for Condensed Matter Timisoara tries to take benefits from both above mentioned methods and to cumulate their advantages, meanwhile eliminating the disadvantages of each of them.

The equipment consists mainly from (i) a domestic microwave oven (modified for a continuous microwaves radiation power adjustment capability) which contains (ii) the autoclave with the growth medium which has attached (iii) the ultrasonication device.

There are two possibilities to apply the ultrasonic energy to the solution. In one of them, the ultrasonic transducer of PZT type is fixed on the bottom of the autoclave (if such be the case, through a $\lambda/2$ lengthener piece to avoid overheating of the piezoceramics). Through the superior lid of the autoclave one introduce tightly a thermocouple's plunger which permits temperature measurement and control. (Fig.1)

Another tested constructive possibility is with immersed sonothrode, namely the sonothrode passes through the superior lid of the autoclave (the passing and tightening region is around a nodal point of the sonothrode), and the thermocouple passes through the bottom of the autoclave. (Fig.2) The advantage of this configuration is a smaller ultra acoustic energy needed to

obtain cavitations, but sealing problems can occur.

Of course, it is of real interest to try measuring/controlling the temperature inside the autoclave by means of a non-contact IR thermometer; this will be the next step in our research.

The equipment works as follows: (Fig.1)

One fills the autoclave with growth solution (which can be Titanium izopropoxy or amorphous gel $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, etc for Titania nanocrystals, by example), in 60%-80% proportion. The autoclave-sonothrode assembly is introduced into the microwave oven, the PZT transducer remaining outside of the oven to avoid the interferences between them.

The bottom of the autoclave is metallic (if needed, lined with a thin Teflon layer for chemical stability), so it can transmit easily the ultrasonic energy from the PZT to the solution. Being from massive metal, both the metallic bottom lid and the sonothrode will reflect the microwaves, so no negative influences occurs. In regular domestic or industrial MW ovens, the heated pieces are continuously rotated around a central vertical axis in order to achieve a homogeneous heating. In our case, it's very difficult to rotate the assembly autoclave-sonothrode-PZT inside the oven. Therefore, to avoid the formation of stationary waves in the oven and unwanted «hot spots» in the solution, one must introduce a «radiation stirrer». Basically, it is about a metallic paddle conveniently oriented to the radiation source (magnetron, 2.45 GHz, max 1000W) which rotates around its axis. In this way, the waves reflected from the oven's walls, the paddle and the metallic parts of the autoclave will change permanently, avoiding stationary waves formation inside the oven.

When starting the heating, with full power in order to achieve as quickly as possible desired temperature, one starts also the ultrasonic generator (power 0-750W, and 20 kHz to 40 kHz frequency, depending on autoclave's geometry). This will ensure an effective solution agitation and therefore a uniform solution heating. Once the working temperature is achieved (very shortly, in tens of seconds or maximum few minutes) one reduce the emitted microwave power in order to maintain a constant temperature inside the autoclave as long as required. The process can be automated, the temperature being

controlled by the means of a thermocouple or an IR Pyrometer and a temperature controller.

When the crystallization process is over, by simply opening the oven's door or vigorously ventilating the interior, one can quickly cool down the vessel, dramatically reducing the necessary time for one complete synthesis.

The advantages of this combined method over each individually above mentioned are obvious, namely:

- During the process, rapid heating will allow to surpass unwanted transitory phenomenon and unwanted premature crystallizations. Because the microwave radiation and ultrasonic field, the reaction kinetics are several times improved, and the agitation due to ultrasonic waves ensures a good homogenization in the solution, a good temperature uniformity in the autoclave and prevents the conglomerates development.

- Total time consumption for a complete synthesis is considerably reduced, by several times. In this way, dozens of synthesis can be performed every day, instead of max 2-3 by conventional ultrasonic assisted hydrothermal method.

- Cooling quickly the system is a very simple procedure, only by a vigorous ventilation, without need to manipulate the hot pressurized vessels, which could be dangerous. In the classical hydrothermal procedures, for a quick cooling, the hot autoclave has to be removed from the warm electrical oven, which could expose the personnel to some risks.

- The new formed nanocrystals are not any more decanting on the autoclave's bottom because the ultrasonic stirring, so all the particles are evenly exposed to the solution's nutrients.

- No more conglomerates can be formed because the micro jets and cavitations bubbles implosion. A very narrow dimensional dispersion is achieved.

- The process is environmental friendly; the hermetically closed autoclave avoids any toxic

gases/vapors emissions into atmosphere.

– Because the reduced time of operation, electrical energy consumption is 5-10 times lower than in classical procedures

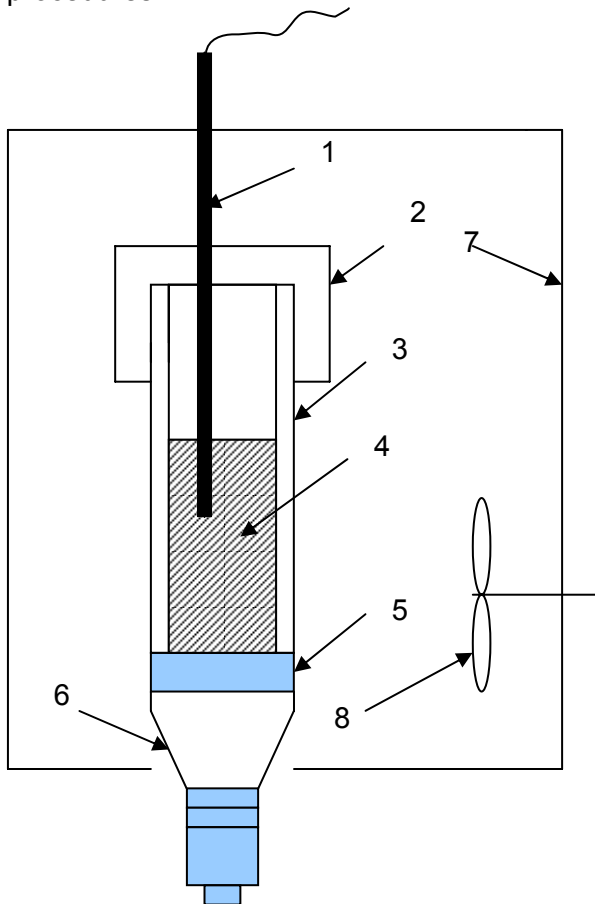


Fig.1

1-Thermocouple; 2-Autoclave's lid; 3-Teflon autoclave; 4-growth solution; 5-autoclave's bottom; 6-piezoceramic transducer-sonothrode assembly; 7-microwave oven (metallic) walls; 8-«radiation stirring» metallic paddle

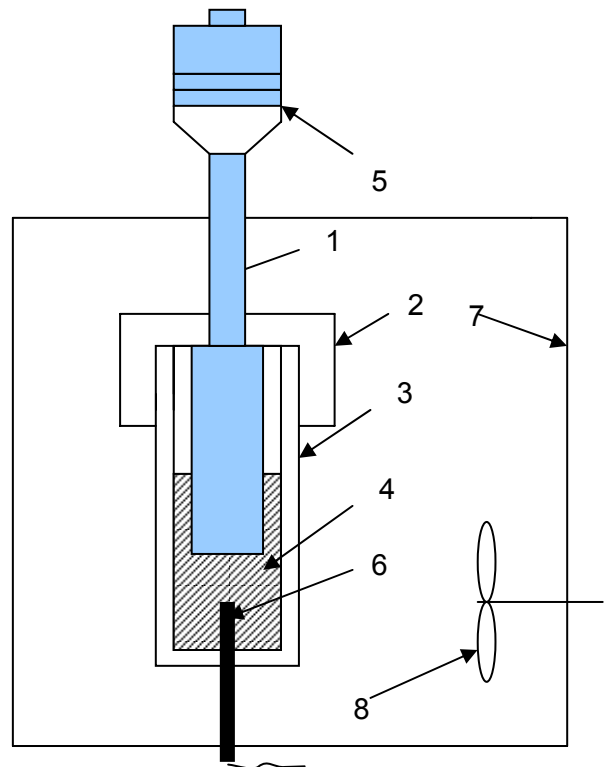


Fig.2

1-Imersed sonothrode; 2-autoclave's lid; 3-teflon autoclave; 4-growth solution; 5-piezoceramic transducer; 6-thermocouple 7-microwave ovens walls; 8-«radiation stirrer»

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