

## THE STUDY OF PREPARATION OF NANOPARTICLES WITH DEFINED PROPERTIES VIA SELF COMBUSTION SYNTHESIS

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### Abstract

Self-combustion synthesis (SCS), a method of production of fine ceramic particles by burning suitable metallic precursors with organic fuel in a presence of an oxidizing agent, is an easy to use, high yield method, that, when mastered, can lead to production of significant amounts of nanoparticles with tuned properties and morphology. The method was used to prepare fine particles of iron oxide, cerium oxide, praseodymium oxide and various other lanthanide oxides with different organic fuels, including glycine, citric acid, ethylene glycol, urea and starch. As metallic precursors, nitrates and organic complex compounds were used. In summary, all particles produced by self-combustion synthesis form, apart from separated nanoparticles, slightly larger agglomerates with dimensions of up several micrometers. The nano-sized grains, however still remain apparent. Further experiments were also made with electrospinning the precursors into nanofibers with carrier polymer prior to calcination, so those would preserve the morphology during the process. Electron microscope pictures show, that by using nitrates as precursors, the resulting oxidic fibers retain a smooth surface, while the use of organic complex compounds yields highly porous structures, some of which retain the general fibrous structure, depending on the carrier polymer and rate of heating. A formation of porous structures was generally observed for most of the organic complexes and fuels.

**Keywords:** Lanthanides, oxides, citrate, self-combustion, rare earth

### 1. INTRODUCTION

Oxidic particles with grain dimensions under 100 nm exhibit significantly different properties, compared to their macro-scale counterparts, mainly thanks to their enormous surface area. Furthermore, nanoparticles of heavy metals are nowadays one of the dominant areas of research. Lanthanide oxides nanoparticles exhibit excellent properties as catalysts, radiation absorbers or as components of fuel cells.

This work deals with the problematic of preparation of heavy metal oxides nanoparticles with focus on lanthanide-series elements. The focus is to use environmentally safe, inexpensive and commonly available precursors, while achieving high yields of oxidic nanoparticles with dimensions under 100 nm with as narrow as possible size distribution, to be used for production of hybrid polymer nanocomposite materials for radiation shielding. While this is a very popular topic, the sources only rarely deal with productivity of the process and leave a lot of unanswered questions (i.e. the temperature optimization). The materials produced were examined chiefly by scanning electron microscopy (SEM).

### 2. EXPERIMENTAL

The stock oxidic materials were first converted into nitrates, water soluble and easier to process compounds. Using several different methods, oxidic nanoparticles were obtained via several different routes, while being focused on self-combustion synthesis (SCS).

## 2.1. Materials

As a precursor for cerium oxide particles, cerium nitrate hexahydrate (>99 %) was purchased from Sigma-Aldrich. Ferric oxide nonahydrate was purchased from Penta, Ltd. Oxides of lanthanides were obtained from company Crytur, Ltd. As the company deals with growth of highest quality monocrystals, the materials were used without further purification. Glycine (>99 %, Reanal), citric acid (99.8 %, Chemapol) were used. Any other chemicals were used as they were from the standard lab supplies.

## 2.2. Instrumentation

For experiments, magnetic stirrer MR Hei (Heidolph), hot air drier UM 500 (Mettler) and programmable furnace L3S27 (Nabertherm) were used. The characterization was carried out using Vega 3 scanning electron microscope (Tescan) and FE-SEM Ultra Plus (Zeiss) in the Laboratory of analytical methods of Technical university of Liberec.

## 2.3. Precursors preparation

The compositions of the prepared reaction mixtures are based on a number of references, including [1-5], but have been further optimized according to our previous observations of the experiments [6] and theory of complexation chemistry [7].

Nitrates of lanthanum, praseodymium, neodymium, erbium and gadolinium were prepared from the according oxides. Oxides were dissolved in slightly higher than equimolar amount of concentrated nitric acid at temperatures between 50 and 60 °C. When fully dissolved, the solutions were left to dry at temperature of 60 °C. When dried, the samples were stored in dry environment and sealed against atmospheric humidity until further processed.

As fuels for the synthesis, citric acid, glycine and urea were used. For experiments with citric acid, 1 gram of the nitrate (in hydrated form) of each element was dissolved in 20 ml of distilled water. 1.5 grams of citric acid were then slowly added to the solutions during continuous stirring. Solutions were then mixed thoroughly and left to dry in atmospheric conditions at 80°C overnight.

Similar procedure was carried out with glycine. 1 gram of each nitrate was dissolved in 20 ml of distilled water, along with 1 gram of glycine. After thorough mixing, the solutions were left to dry overnight in atmospheric conditions at 80°C.

1 gram of each of the nitrates was dissolved in 20 ml of distilled water. 0.7 grams of urea were then added to the solutions. After mixing, the solutions were left to dry overnight at 80°C.

## 2.4. Self-combustion synthesis

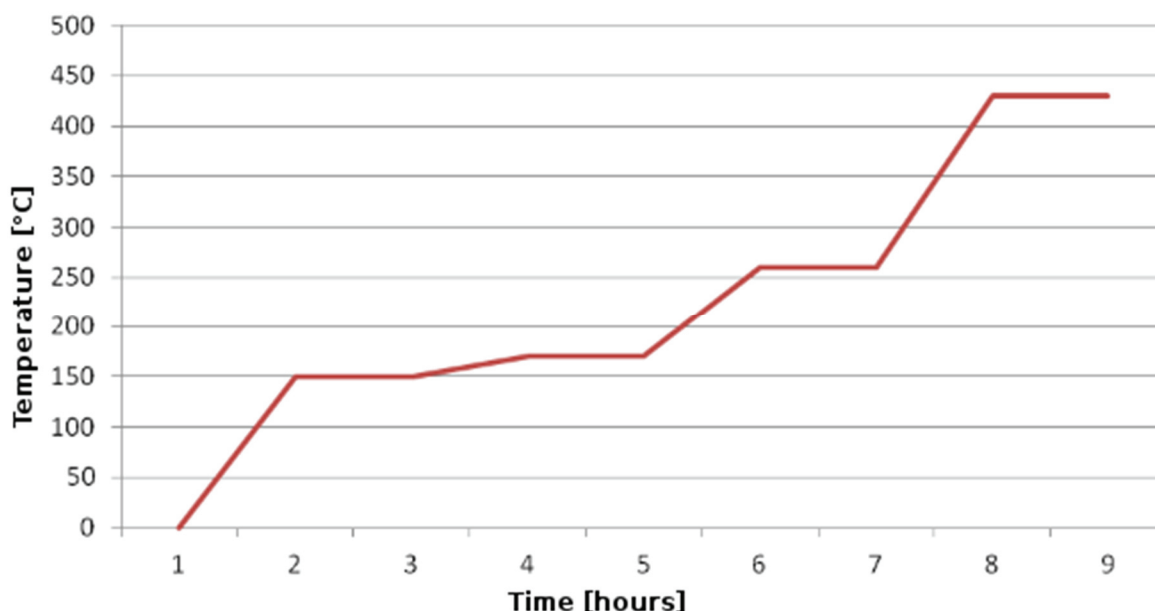
The time-temperature profiles used for the SCS method have been optimized according to previous observations and experiments [6] and thermogravimetric analysis of the precursors.

The dried samples with citric acid complexes were heated in a glass beaker to the temperature of 430°C. The time-temperature profile used is shown in **Figure 1**. At temperatures over 260°C, combustion was observed. During this stage, fine nanoparticles are supposed to form [1]. After reaching 430°C, the samples were transferred into ceramic crucibles and calcined at 650°C for 2 hours.

After drying, the samples with glycine formed a glass-like surface at the bottom of the beaker. Beakers with samples were then heated same way as with citric acid. The combustion was observed at similar temperatures as well. The samples were then transferred into ceramic crucibles and calcined at 650°C for 2 hours.

The appearance of samples with urea was very similar to those with glycine. The layer was however a bit more brittle and it was possible to easily break it down into smaller pieces. The process of self-combustion was almost the same as for other samples. After being transferred into ceramic crucibles, the temperature was

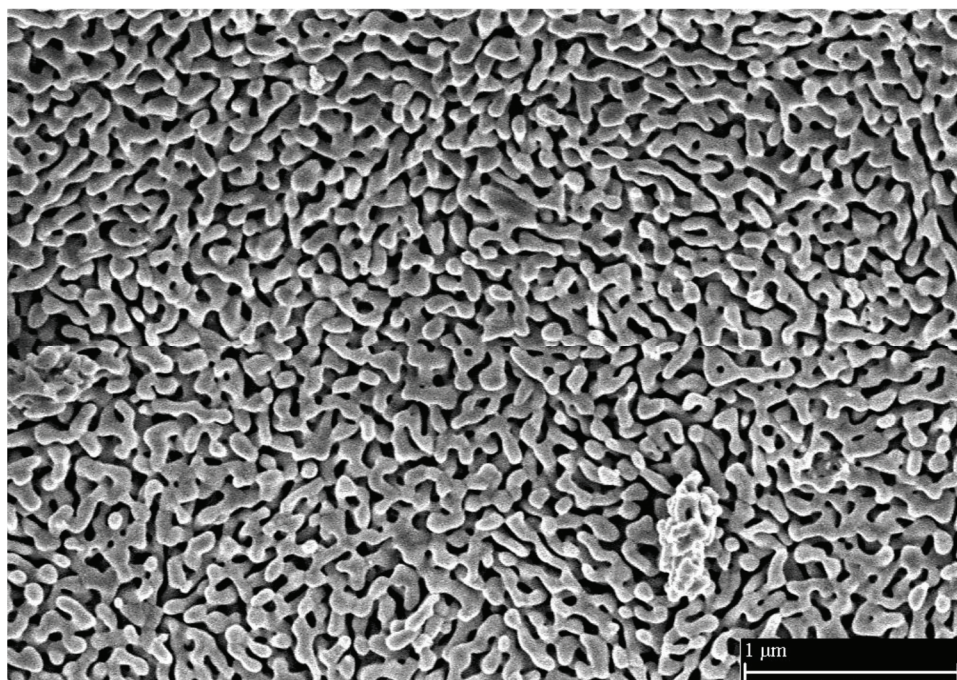
gradually increasing and after 2 hours it reached 650°C. The temperature was then kept constant for an hour before cooling down.



**Figure 1** Diagram of temperatures used for self-combustion synthesis up to 430°C

### 3. RESULTS

In case of lanthanides, using citric acid as fuel yields high amounts of fine particles. There is however a large number of agglomerates, which can be further broken down by mechanical grinding. In case of iron oxide, the resulting particles were quite homogenous and, although agglomerated as well, the individual particles are still easily distinguishable and assume a “worm-like” structure (**Figure 2**).



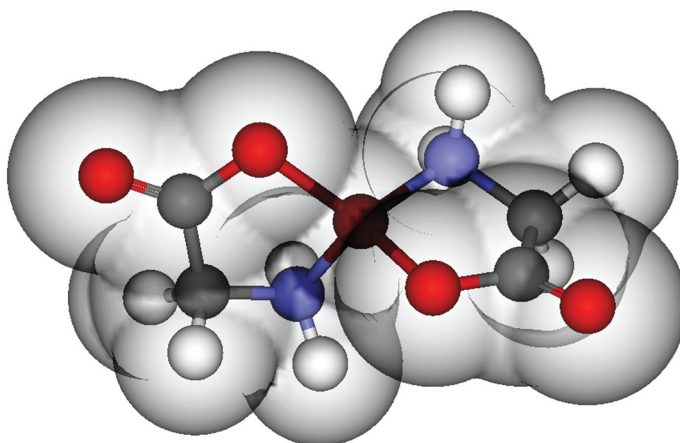
**Figure 2** Iron oxide nanoparticles, obtained by SCS method using citric acid and iron nitrate. Scale is 1 μm.

When using urea as fuel, lanthanides oxides generally formed agglomerates composed of distinguishable particles with dimensions around 100 nm. These were covered with smaller particles with dimensions around 12 nm. Iron oxides prepared with this fuel were in range of 56 to 170 nm and formed much smaller amounts of agglomerates than in case of lanthanides. The surface of the particles also had a substantial amount of nanoparticles with dimensions under 15 nm.

Using glycine as a fuel yielded porous particles of all used materials. All samples had a thick top layer of sintered material, below which a porous structure unfolded. For lanthanides, walls of the pores were about 20 nm thick, while for iron oxide, this thickness was several hundred nanometers. In lanthanides samples, a number of nanoparticles was observed on the grains of the porous structures. In iron oxide, hexagonal structure of the crystals was distinguishable.

#### 4. CONCLUSION

For self-combustion synthesis, sintered surface layer composed of breakable agglomerates is typical. Under this layer, fine and usually quite homogenous particles can be found. While the lanthanides generally exhibited the same appearance in all cases, the iron oxide samples were either metallic black (urea) or rusty brown (citric acid, glycine). It is very difficult to control the structure and morphology of final product without further investigation into the effect of different fuel to precursor ratios and time-temperature profiles during the calcination process.



**Figure 3** Expected structure of chelate of iron(II) ions with glycine

After evaporating most of the water from the reaction mixtures, rather stable complexes are formed. Those protect the metal ions from hydrolysis and separate them, so agglomerates too early in the process. Existence of these agglomerates has before been proven and even their stability constants were measured [7]. The reaction mixture therefore has to have the optimal composition to form the protective chelate complexes that can withstand increased temperatures. We expect, that in the beginning of the heating process, fuel molecules are slowly released and the complexes bridge to one another, while slowly nearing the combustion temperature. After the combustion of the reaction mix, the complexes are broken down quickly and oxidic particles are formed. Expected form of the chelates is similar to the usual glycine complexation, as shown in **Figure 3**.

Despite its shortcomings, SCS method generally provides high yields with over 90% conversion rate and efficiency (losses mainly due to manipulation). In our experiments, we have also tested microemulsion method of preparing the oxidic nanoparticles, which yielded a narrow, uniform particle size distribution, however with very low yields. For our purposes, the method described is much more suitable, as monodispersity is not strictly required. A high purity of the products is easily achievable, as the organic impurities are removed during the



calcination process. This also enables the use of budget-friendly, lower purity reagents as fuels, keeping down the cost of final products.

## ACKNOWLEDGEMENTS

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