

# CONTINUOUS HYDROTHERMAL SYNTHESIS OF $\text{Co}_3\text{O}_4$ NANOPARTICLES IN SUPERCRITICAL WATER

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## Introduction

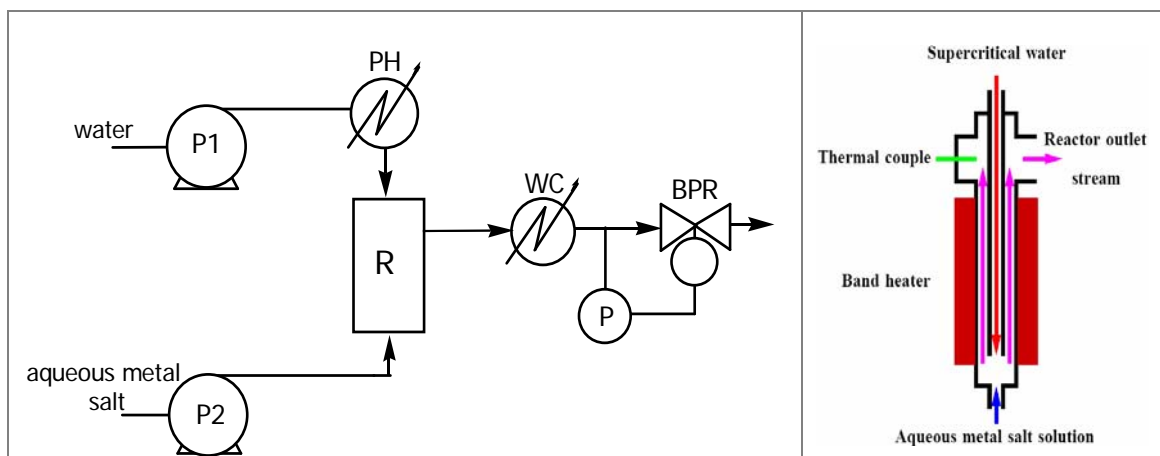
Hydrothermal synthesis of metal oxide nanoparticles in sub or supercritical water is a rapid and relatively simple method pioneered by Adschiri and co-workers and is based on the extremely low solubility of inorganic compounds in water near or above its critical point [1,2]. The drastic changes in the density, dielectric constant and ionic product of water around its critical point (374 °C, 221 bar) result in the formation of fine crystalline metal oxide nanoparticles by simply mixing a solution of a metal salt with supercritical water. As the result, the hydrolysis of the metal salt occurs spontaneously, rapidly followed by dehydration.

Many applications of metal oxide nanoparticles require particles to be of a certain size as the unique properties of nanoparticles are size related. Therefore, the ability to perform size-controlled synthesis is of great importance.

In this paper, we present the results of continuous hydrothermal synthesis of cubic  $\text{Co}_3\text{O}_4$  nanoparticle suspensions and improve of the  $\text{Co}_3\text{O}_4$  nanoparticle size. The influence of reaction conditions such as water temperature, metal salt concentration and changes in the flow rates on the particle size have been investigated.

## Materials and Methods

The equipment for continuous production of metal and metal oxide nanoparticles (Figure 1) consists of:  $\text{H}_2\text{O}$  pump (Gilson HPLC piston pump 305 model, 25 SC pump head), a pump for the metal salt solution (Gilson HPLC piston pump 305 model, 10 SC pump head), an electrical heater (1KW), a water cooler and a computer controlled Tescom back-pressure regulator (BPR: Model 26-762-46). The hydrothermal synthesis is performed in a nozzle type reactor (Figure 2.) by mixing supercritical (or sub-critical) water with aqueous metal salt solution at room temperature [3]. In this apparatus, water is pumped through an electrical heater where it is heated to the required temperature and is then fed downwards to the reactor through the central pipe which ends in a nozzle. The aqueous metal salt solution is fed at the room temperature counter-currently upwards through the outer pipe. The two streams are mixed nearly instantaneously and nanoparticles are formed. The reaction product pumped through the reactor outlet is immediately cooled by the water cooler and collected after exiting via the BPR which maintains and controls the system pressure.



**Figure 1.** Flow diagram of the continuous supercritical water reactor system: P1 and P2 – Gilson HPLC pumps, PH preheater, R- continuous flow reactor, WC –water cooler, BPR – Tescom back pressure regulator, P – pressure transducer

**Figure 2.** The Nozzle reactor [3]

The hydrothermal synthesis of  $\text{Co}_3\text{O}_4$  nanoparticles was carried out from two starting solution: aqueous cobalt salt and dilute hydrogen peroxide. Cobalt (II) acetate tetrahydrate (98%, Sigma Aldrich) salt was dissolved in dionised water at the room temperature. This solution was prepared immediately before the synthesis. The experiments were carried out at three different concentrations (0.01 M, 0.03 M and 0.05 M) of cobalt (II) acetate tetrahydrate (later called precursor) in order to analyze effect of the precursor concentration on particles size. The second solution was prepared by adding hydrogen peroxide (Fisher, 30 % 100 vol.) to  $\text{H}_2\text{O}$  ( $25 \text{ ml l}^{-1}$ ).  $\text{H}_2\text{O}_2$  was needed to create unoxidizing environment in order to obtain  $\text{Co}_3\text{O}_4$  nanoparticle. The dilute solution of  $\text{H}_2\text{O}_2$  decomposes thermally  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the heater by thermal decomposition of  $\text{H}_2\text{O}_2$  what was previously reported and confirmed in the research work at Nottingham [4,5]. This allows the mixture of  $\text{O}_2$  and  $\text{H}_2\text{O}$  to be fed to the reactor at sub or supercritical conditions.

In this work, we compare results obtained with water at temperatures of  $300^\circ\text{C}$  and  $430^\circ\text{C}$  and at 230 bar pressure. These temperatures are those of water at the reactor inlet and will be referred as reaction temperatures. During the experiments at  $300^\circ\text{C}$ , the flow rates were  $20 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $10 \text{ ml min}^{-1}$  for the salt solution, with a residence time 3.3 s. In the experiments at  $430^\circ\text{C}$ , two different flow rates were chosen: one with  $20 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $10 \text{ ml min}^{-1}$  for salt solution and a residence time of 0.5 s and the second with  $3 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $1.5 \text{ ml min}^{-1}$  salt solution with a residence time of 3.3 s. The values of the residence time were calculated rather than measured. Each experiment was repeated performed in triplicate.

The nanocrystals were characterized by powder X-ray diffraction (XRD, Philips EXPERT 1830 diffractometer). The samples for analysis were prepared by freeze-drying at  $-50^\circ\text{C}$  under the vacuum. Nanoparticle sizes were determined from images obtained by Transmission Electron Microscopy (TEM, JEOL JEM-200FXII).

## Results

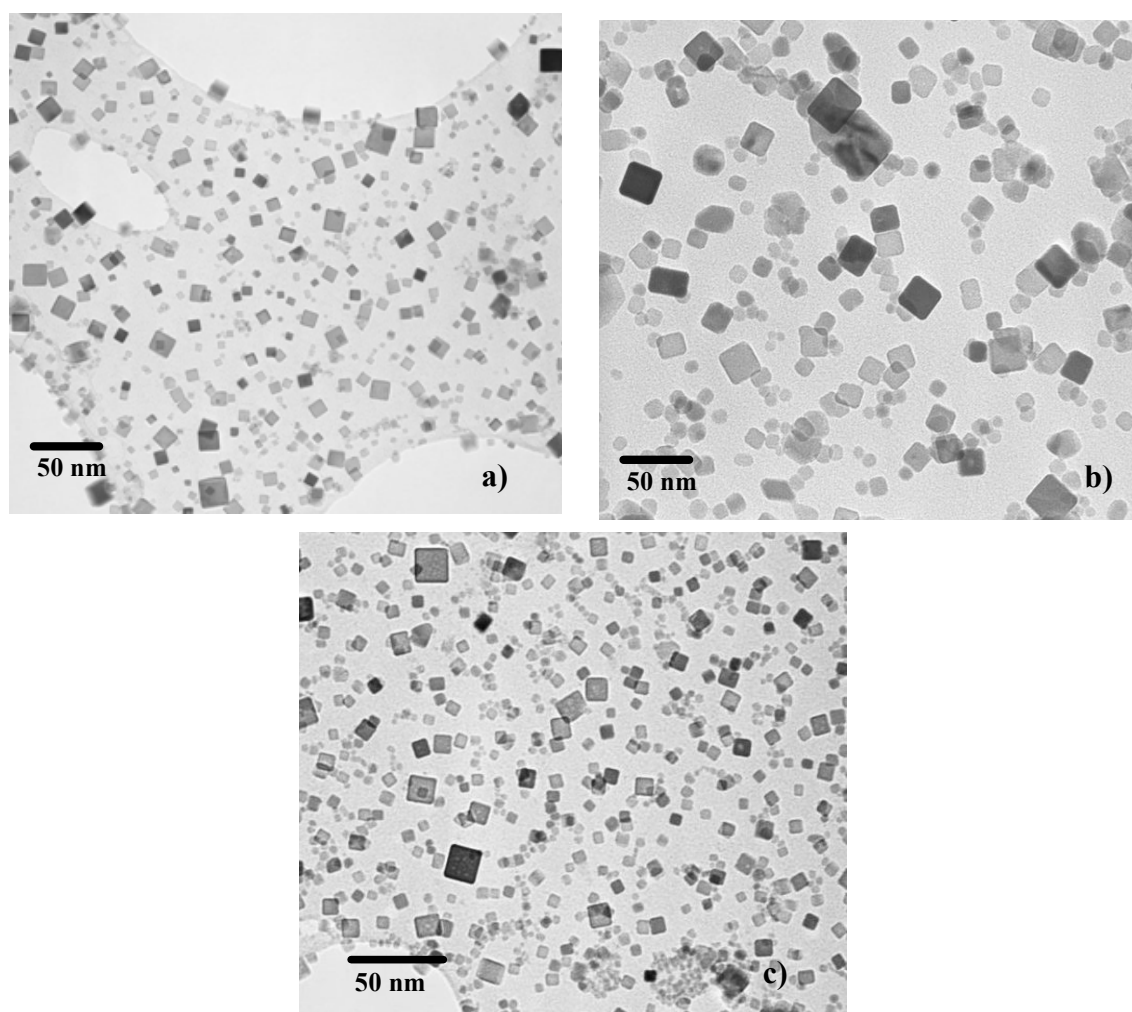
The size of the obtained nanoparticles synthesized in the continuous flow hydrothermal synthesis apparatus varied between 6 and 90 nm depending on the experiment condition. The reaction conditions and average particles size are summarized in Table 1.

**Table 1.** Size average of  $\text{Co}_3\text{O}_4$  nanoparticles obtained under different reaction conditions

$T_C$	Concentration of cobalt	Flow rates for $\text{H}_2\text{O}/\text{O}_2$ and salt	$\text{Co}_3\text{O}_4$ particle size
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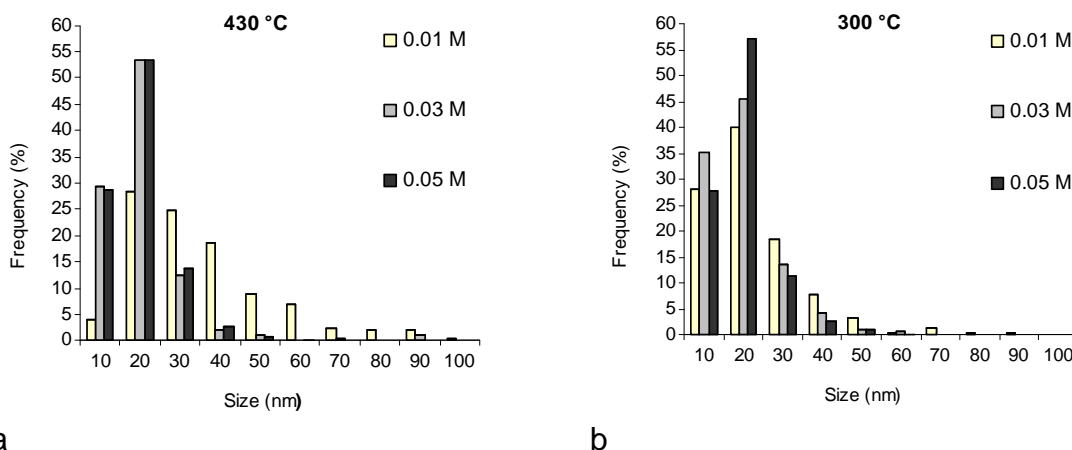
	(II) acetate tetrahydrate	solution	average (nm)
300 °C	0.01 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	18
	0.03 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	14.5
	0.05 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	14.1
430 °C	0.01 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	36
	0.01 M	3 ml min <sup>-1</sup> and 1.5 ml min <sup>-1</sup>	25
	0.03 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	15.5
	0.05 M	20 ml min <sup>-1</sup> and 10 ml min <sup>-1</sup>	15
	0.05 M	3 ml min <sup>-1</sup> and 1.5 ml min <sup>-1</sup>	8.8

Particles of 10 – 20 nm (Figure 3) size formed the largest percentage of all the particles independent of the precursor solution concentration and the reaction temperature.



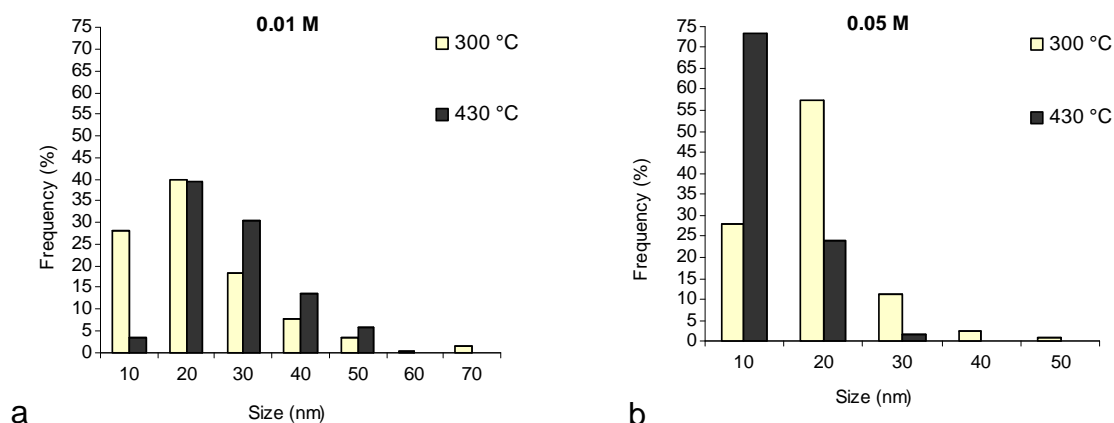
**Figure 3.** TEM pictures of  $\text{Co}_3\text{O}_4$  nanoparticles synthesized at from 0.05 M of metal salt precursor at: a) 300 °C and at the flow rates of 20 ml min<sup>-1</sup> for  $\text{H}_2\text{O}/\text{O}_2$  and 10 ml min<sup>-1</sup> for salt solution, b) at 430 °C and the flow rates of 20 ml min<sup>-1</sup> for  $\text{H}_2\text{O}/\text{O}_2$  and 10 ml min<sup>-1</sup> for salt solution, c) at 430 °C and the flow rates of 3 ml min<sup>-1</sup> for  $\text{H}_2\text{O}/\text{O}_2$  and 1.5 ml min<sup>-1</sup> for salt solution.

However with regard to particle size distribution, higher concentrations of cobalt (II) acetate tetrahydrate gave a smaller average particle size with a narrower size distribution at both 300 °C as well as at 430 °C. The  $\text{Co}_3\text{O}_4$  nanocrystals with widest size distribution were synthesized from 0.01 M cobalt (II) acetate tetrahydrate. Smaller nanoparticles with a narrower size distribution were obtained from 0.05 M cobalt (II) acetate tetrahydrate (Figure 4).



**Figure 4.** Size distribution of  $\text{Co}_3\text{O}_4$  nanoparticles synthesized from 0.01 M, 0.03 M and 0.05 M concentrations of cobalt (II) acetate tetrahydrate (a) at 300 °C and (b) at 430 °C.

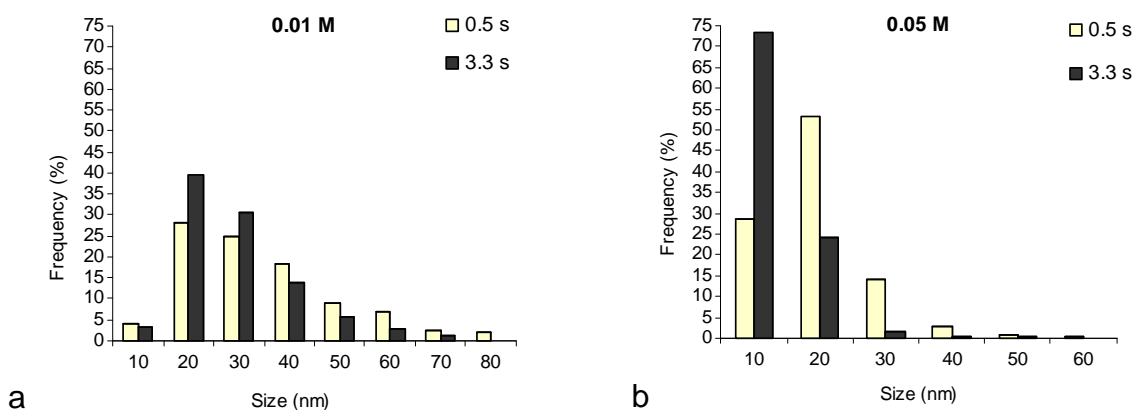
The reaction temperature above the critical point effects decrease in size of  $\text{Co}_3\text{O}_4$  nanoparticles, compared to those synthesized at subcritical temperatures. Particles obtained from the 0.05 M precursor were smaller when synthesis was carried out at 430 °C rather than at 300 °C (Figure 5). However, the temperature effect was less significant for particles synthesized from the 0.01 M precursor.



**Figure 5.** Size distribution of  $\text{Co}_3\text{O}_4$  nanoparticles synthesized (a) from 0.01 M and (b) from 0.05 M cobalt (II) acetate tetrahydrate.

The effect of flow rate on particle size was investigated at 430 °C. Our results show that, at the higher flow rate ( $20 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $10 \text{ ml min}^{-1}$  for salt solution) with a residence time of 0.5s, larger nanoparticles were obtained; while at lower flow rates ( $3 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $1.5 \text{ ml min}^{-1}$  for salt solution) with the residence time of 3.3 s, gave smaller particles (Figure 6). The effect of the flow rate on the final particle size was more significant for particles obtained from the higher salt concentration.

When the synthesis was carried out from the 0.01 M precursor, the largest percentage of particles were 10 – 20 nm in size. The reduced flow rates effected a narrower size distribution but the largest number of particles remained 10 – 20 nm of size. However, when the 0.05 M precursor was used, the reduced flow rates resulted the formation of smaller particles. At flow rates of  $20 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $10 \text{ ml min}^{-1}$  for salt solution, the largest percentage of particles were 10 – 20 nm in size, but when flow rates were  $3 \text{ ml min}^{-1}$  for  $\text{H}_2\text{O}/\text{O}_2$  and  $1.5 \text{ ml min}^{-1}$  for salt solution, the largest percentage of particles were 5 -10 nm in size, with narrower size distribution.



**Figure 6.** Size distribution of  $\text{Co}_3\text{O}_4$  nanoparticles synthesized at different residence time from 0.01 M cobalt (II) acetate tetrahydrate (A) and from 0.05 M (B) at 430 °C.

### Conclusions

Our experiments show that this approach gives highly crystalline  $\text{Co}_3\text{O}_4$  nanoparticles. They also suggest that, for a given reactor, the precursor concentration has an influence on the particle size and size distribution. A higher concentration (0.05 M) of cobalt (II) acetate tetrahydrate precursor gives rise to decreased particle size both at 300 °C and at 430 °C water temperatures. An increase in reaction temperature from 300 °C to 430 °C appears to have a somewhat more significant effect in decreasing particle size, when particles were synthesized with a higher (0.05 M) concentration of the precursor. A similar effect was observed by analyzing the influence of flow rate. When the synthesis was carried out at 430 °C, a decrease in the flow rates significantly affected particles synthesized from higher precursor concentration (0.05 M) and has less effect in case of lower concentration (0.01 M). However, it should be remembered that changing the residence time via changing the flow rates of the fluids also changes the Reynolds Number and, hence, the degree of mixing in the reactor. Experiments are now in progress to investigate the effect of Reynolds Number on particle size.

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