

# **Continuous hydrothermal synthesis of polymer-coated Fe<sub>2</sub>O<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles**

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## **ABSTRACT**

Metal oxide nanoparticles are of practical interest in a variety of applications including high-density information storage [1], magnetic resonance imaging [2] and targeted drug delivery [3]. Many of these applications require particles of predetermined size and narrow size distribution. Processes that lead to particles with these characteristics are therefore of considerable interest. Cobalt ferrite, CoFe<sub>2</sub>O<sub>4</sub>, is a well-known hard magnetic material with very high cubic magnetocrystalline anisotropy, high coercivity, and moderate saturation magnetization [4], which makes it a promising material for high-density magnetic recording.

We have previously [5-7] reported on the continuous hydrothermal synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, and CoFe<sub>2</sub>O<sub>4</sub> particles and shown that speciation and solubility play a key role in the production of these oxides. Particle agglomeration, however, was a key limitation in these studies. Aggregation and growth of such particles can be avoided (1) by coating the nanoparticles with a protective layer; (2) by fixing the particles to a substrate; or (3) by precipitating the particles in a confined space [8, 9].

In the present work, we have employed a continuous hydrothermal technique for the synthesis of PVA-coated Fe<sub>2</sub>O<sub>3</sub> and CoFe<sub>2</sub>O<sub>4</sub> nanoparticles. The continuous process allows effective control of particle size because nucleation and growth stages of particle formation are essentially separated. Iron and cobalt ferrite nanoparticles were synthesized in the presence of poly(vinyl alcohol) (PVA) and the results are reported in this work. The effect of experimental conditions on particle size, size distribution, particle morphology, and crystallinity were studied. The particles were characterized by powder x-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques.

## **RESULTS**

### CoFe<sub>2</sub>O<sub>4</sub> particle formation in the absence of PVA

The major product at all conditions (between 473 K and 673 K) was CoFe<sub>2</sub>O<sub>4</sub> with a small amount (approximately 2%) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The average crystallite size was calculated to be ~ 20 nm. Micrographs (Figure 1) showed that the particles were spherical or cubic in morphology, with an average particle size close to the calculated crystallite size and a standard deviation of ~3 nm. The temperature did not seem to have a significant affect on the particle size in the range of temperatures studied, although the residence time also plays a role in these experiments. An increase in the temperature leads to a decrease in the density of the solution, resulting in shorter residence times. This effect is particularly pronounced as the solution goes from sub-critical to supercritical conditions. Shorter residence times resulted in higher weight fractions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in the product.

### CoFe<sub>2</sub>O<sub>4</sub> particle formation in the presence of PVA

Figure 2 shows the transmission electron micrograph of CoFe<sub>2</sub>O<sub>4</sub> particles and the corresponding electron diffraction pattern. The well-defined rings in the diffraction pattern indicates that the particles are crystalline. Figure 3 shows the polymer coating around Fe<sub>2</sub>O<sub>3</sub> particles.

## **CONCLUSIONS**

The continuous hydrothermal technique can be used to produce iron and cobalt ferrite nanoparticles with narrow size distributions. Very small particles are obtained because of the high supersaturations generated when the feed solutions are mixed with hot, compressed water. The particles, however, tend to agglomerate, especially at higher feed concentrations and higher residence times. Agglomeration can be limited in the presence of PVA.

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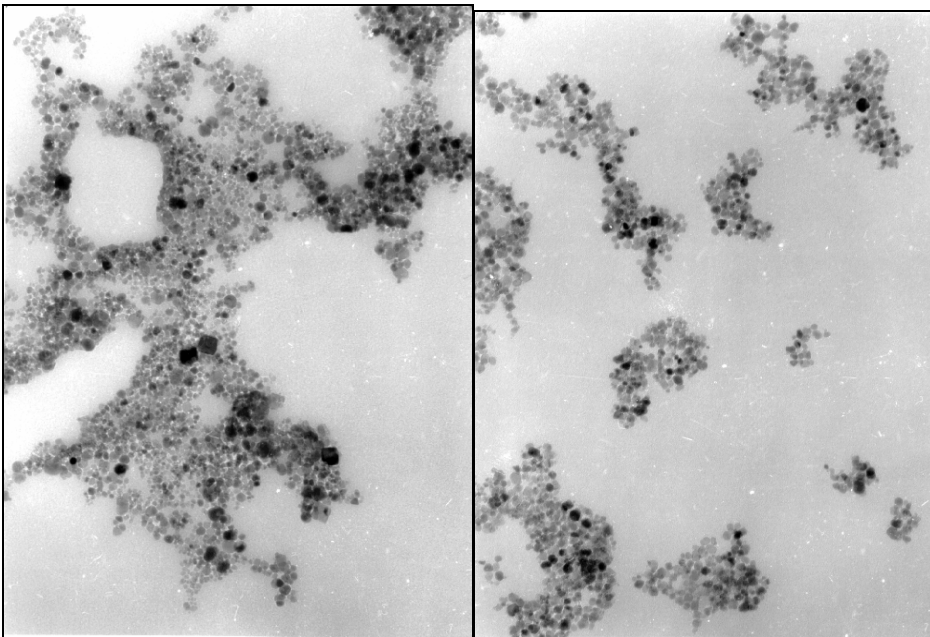


Figure 1 – TEM images of  $\text{Co}_3\text{O}_4$  samples obtained via continuous hydrothermal synthesis

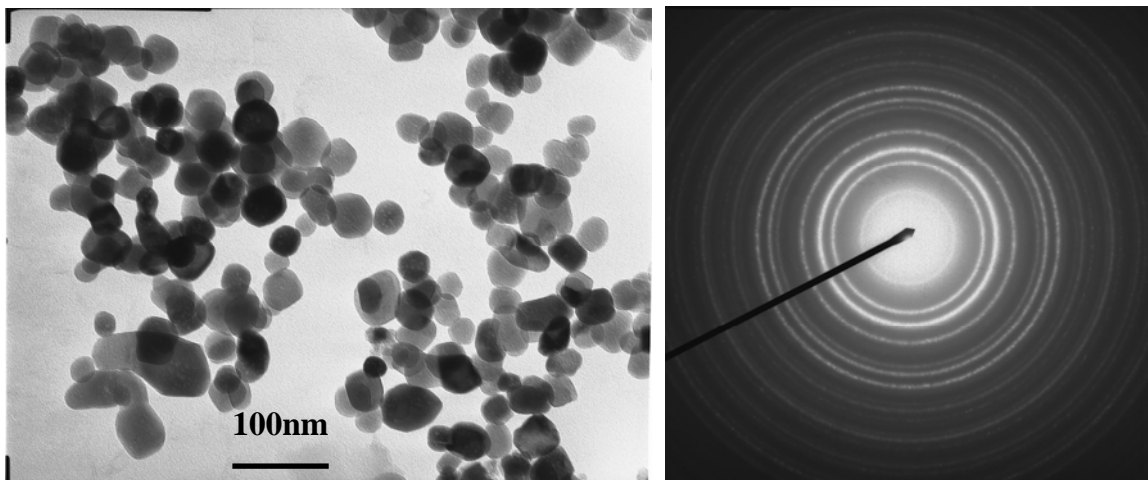


Fig 2. TEM images of  $\text{CoFe}_2\text{O}_4$  nanoparticles in the presence of PVA. Also shown is the corresponding electron diffraction pattern ( $T= 553\text{K}$ , concentrations of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{NaOH}$  are  $0.02\text{ M}$ ,  $0.01\text{M}$ ,  $0.16\text{M}$  respectively;  $[\text{Fe}^{3+}+\text{Co}^{2+}]: [\text{VA}] = 1:1$ )

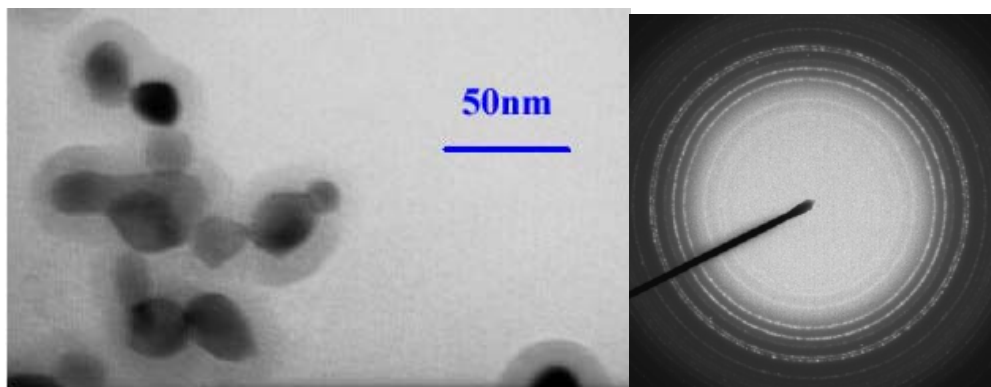


Figure 3. Transmission electron micrograph of PVA-coated  $\alpha\text{-Fe}_2\text{O}_3$  particles and the corresponding electron diffraction pattern ( $T = 300\text{ C}$ ;  $\text{Conc.} = 0.03\text{ M}$ ;  $\text{time} = 10\text{s}$  )