

MS.3.P049

TEM analysis of the influence of the synthetic polypeptide c25-mms6 on the cobalt ferrite nanoparticle growth

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Keywords: Nanoparticles, TEM, EELS

In recent years, biomimetic syntheses of nanoparticles have attracted great interest. Polypeptides play an important role in bio-inspired nanoparticle synthesis, as they are able to control the inorganic crystal growth [1]. To improve our understanding of the interaction between the polypeptide and inorganic crystals, we prepared cobalt ferrite nanoparticle solutions with and without the synthetic polypeptide c25-mms6 [2]. The influence of the polypeptide was investigated by comparing these two sorts of nanoparticles at different growth stages using transmission electron microscopy (TEM) and electron energy loss spectrometry (EELS). The investigations were conducted using an FEI TECNAI G² TF20 transmission electron microscope operated at 200 kV. Figure 1. (left) shows an image of a nanoparticle synthesised with c25-mms6 at a stage where its synthesis is still incomplete. It can be seen that the particle consists of several highly oriented subunits. In Figure 1. (right), a nanoparticle synthesised without the polypeptide is shown for the purpose of comparison. In contrast to the c25-mms6-enhanced particle, no such subunits were observed. Figure 2. (left) shows a hexagonal nanoparticle at the end of its growth process. Additionally, the corresponding diffraction pattern is presented in Figure 2. (right). Only two different orientations are present, namely the [111] and the [-211] zone axes. Together with diffraction patterns acquired at different growth stages, this suggests that the particle surfaces are {111} planes, despite the fact that this plane is usually energetically unfavourable. However, our investigations indicate that the polypeptide c25-mms6 adsorbs onto these specific crystal faces, thus lowering the surface energy. Furthermore, a change of the nanoparticle shape from irregular morphology to hexagonal shape is observed. The composition of the nanoparticles was determined by EELS using a Gatan GIF Tridiem attached to the transmission electron microscope. Quantification of Co and Fe was performed with standard procedures [3]. Analysis of the energy loss spectra shows that using the polypeptide c25-mms6 results in stoichiometric CoFe₂O₄ and Co₂FeO₄ nanoparticles. Without c25-mms6, the nanoparticles consist of non-stoichiometric compositions between Co_{1.3}Fe_{1.7}O₄ and Co_{1.7}Fe_{1.3}O₄. Both approaches have in common that smaller particles are Fe-rich while bigger particles are Co-rich. The results of this study show that the synthetic polypeptide c25-mms6 is not necessary for the formation of cobalt ferrite nanoparticles, but in fact controls the size and phase of the nanoparticles by changing the kinetics of the formation process [2]. It allows the formation of stoichiometric nanoparticles with {111} surfaces.

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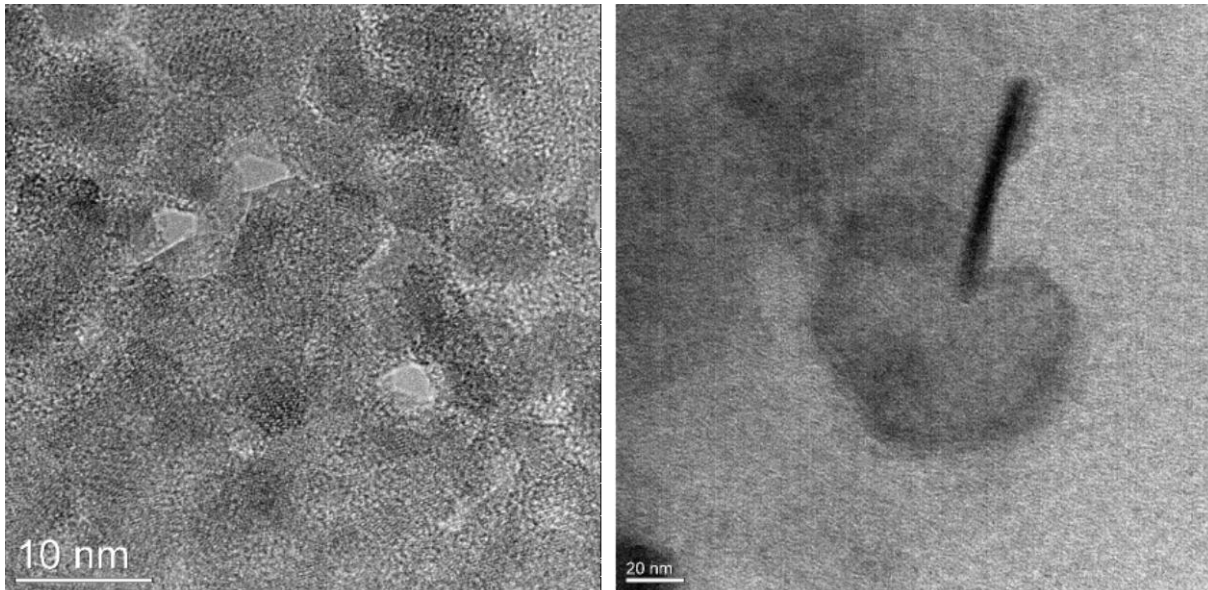


Figure 1. Left: HRTEM image of a nanoparticle synthesised using the polypeptide c25-mms6. The subunits the nanoparticle is formed of can be seen easily. Right: TEM image of a nanoparticle synthesised without the use of c25-mms6.

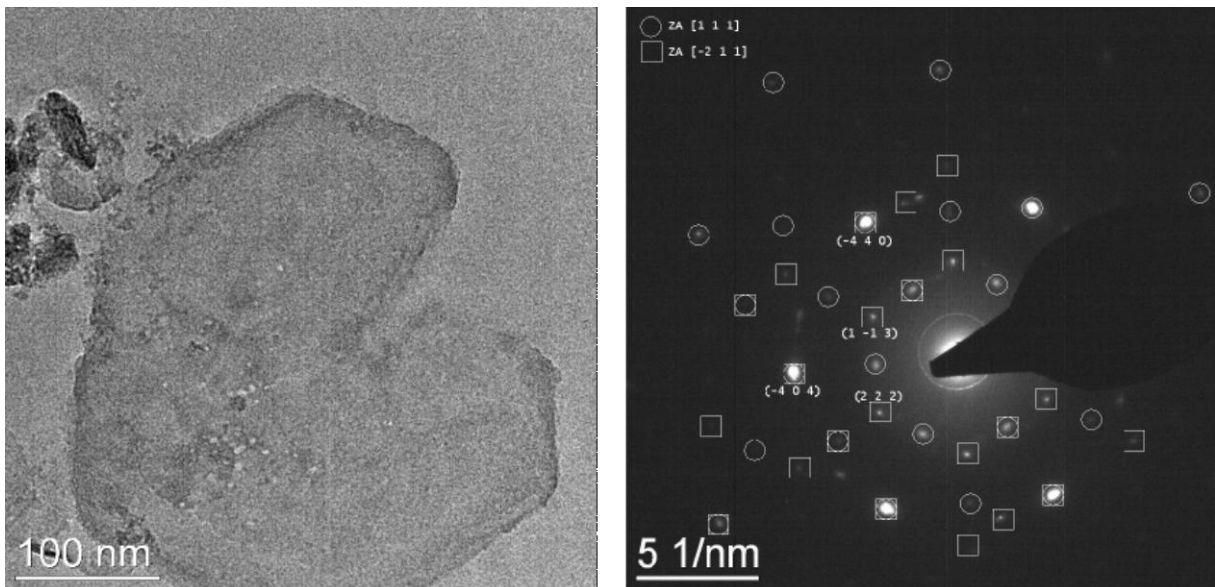


Figure 2. Left: TEM image of a nanoparticle formed by use of c25-mms6 exhibiting roughly hexagonal shape. Right: Corresponding diffraction pattern. The diffraction spots are indexed, only the $[111]$ and the $[-211]$ zone axes (ZA) appear.