Ligand Residues on Fe_2O_3 Nanorods from Hydrothermal Syntheses

Anne S. Schulze[1,2], Claire Günther[1], Natalia Haibel[1], Dirk Walter[1,2]

[1]Laboratories Chemistry and Physics, Institute of Occupational and Social Medicine, Justus-Liebig-University, Aulweg 129, 35392 Giessen

[2]Institute of Inorganic and Analytical Chemistry, Justus-Liebig-University, Heinrich-Buff-Ring 17, 35392 Giessen

Due to its wide range of applications hematite is an attractive material. It can be used, for example, as catalyst[1], pigment[2], gas sensor[3], in lithium ion batteries as anode material[4], in photoelectrochemical cells[5], and for magnetic applications[6]. Hematite is also nontoxic, environmentally sustainable, inexpensive, and relative stable, which adds to its attractiveness.

One-dimensional Fe_2O_3 nanoparticles (NPs) such as nanorods, nanotubes and nanowires, are interesting for electrochemical applications since it was shown that they could improve the electrochemical efficiency of the otherwise low conducting material. These nanostructures can be synthesized using various methods, like sol-gel processes, vapor deposition, template-based syntheses or hydrothermal methods.[7,8]

In a hydrothermal approach, $FeSO_4 \cdot 7H_2O$ and sodium acetate were used to synthesize hematite nanorods. In a first step, α-FeOOH nanorods were formed from the precursors which were heated in a second step at 250 °C for 2 h to obtain the final product.

Sodium acetate acts a base which increases uniformly the pH value of the solution leading to a homogenous nucleation process and therefore, to less polydispersity of the nanorods. It is also possible that it plays a role in the rod formation.[9]

Thermogravimetric (TG) analyses provide the possibility to trace the reaction process from goethite to hematite. In addition, TG measurements were used to validate the quality of the hematite particles. Since impurities can influence the properties, quality control is important. As comparison commercially purchased spherical hematite nanoparticle (< 50 nm) were stirred in a sodium acetate solution, washed and dried.

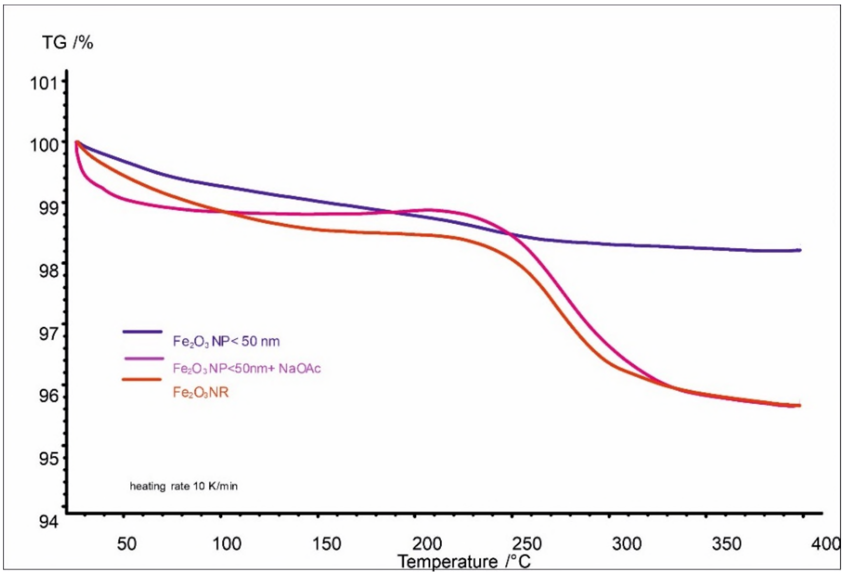

Figure 1: TG measurement of the Fe_2O_3 nanorods (Fe_2O_3NR) and the commercially purchased hematite nanoparticle with (Fe_2O_3NP<50nm+NaOAc) and without (Fe_2O_3NP<50nm) sodium acetate treatment.

The TG measurement revealed that sodium acetate is still present on the surface of the hematite nanorods, despite washing the α-FeOOH NPs in the first step and the heating them afterward. The TG curves of the commercially purchased hematite NPs show a similar progression (Fig. 1). There are two weight loss steps visible. The first step up until 180 °C can be assigned to desorption of the physically adsorbed water on the surface of the particles. The second step up until about 310 °C arises from the decomposition of the acetate.

The results show that acetate ligands are stable on the surface of hematite nanoparticle for temperatures below 300 °C.

[1] R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, *Science*, **2013**, *342*, 1073–1076.

[2] N. Pailhé, A. Wattiaux, M. Gaudon, A. Demourgues, *Journal of Solid State Chemistry*, **2008**, *181*, 2697–2704.

[3] S. Zolghadr, K. Khojier, S. Kimiagar, *Materials Science in Semiconductor Processing*, **2016**, *54*, 6–13.

[4] X. Wu, W. Wua, Y. Zhou, X. Huang, W. Chen, Q. Wanga, *Powder Technology*, **2015**, *280*, 119–123.

[5] A. Annamalai, P. S. Shinde, T. H. Jeon, H. H. Lee, H. G. Kim, W. Choi, J. S. Jang, *Solar Energy Materials & Solar Cells*, **2016**, *144*, 247–255.

[6] H. Wu, G. Wu, L. Wang, *Powder Technology*, **2015**, *269*, 443–451.

[7] H. Liu, G. Wang, J. Park, J. Wang, H. Liu, C. Zhang, *Electrochimica Acta*, **2009**, *54*, 1733–1736.

[8] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim; H. Yan, *Advanced Materials,* **2003**, *15*, 353–389.

[9] B. Tang, G. Wang, L. Zhuo, J. Ge, L. Cui, *Inorganic Chemistry*, **2006**, *45*, 5196–5200.