Microstructural and Magnetic Properties of Hematite Submicron Pseudo-Cubes Obtained by Nanocrystal Oriented Attachment

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Abstract

Crystal growth does not always occur by atom-by-atom or molecule-by-molecule addition. Studies of nanoscopic and submicrometric materials have revealed that they frequently grow through the self-organization of nanoparticles. Indeed, when these *nanoelements* are faceted single-cystals, their spontaneous aggregation often results in the oriented attachment into complex structures with pseudo-monocrystalline features and unusual physical properties [1-6].

Although it has been shown that a large variety of nanostructured materials grow by oriented attachment mechanism, it seems that nanostructures of certain materials (such as TiO_2 [1], CuO [2], α-Fe_2O_3 [3], ZnO [4], CdSe [5] and PbSe [6], among others) are more conducive to be formed in solution by this crystal growth mode. Therefore, these materials particularly represent excellent experimental models to investigate the oriented attachment growth phenomena and the correlation between microstructure and optical, mechanical, electrical and magnetic properties. In this matter, very recently works have shown that oriented attachment of hematite (α-Fe_2O_3) nanocrystals can lead to the formation of nanostructures with interesting properties and many morphologies, including cubes [7], spindles [3], hollow spindles [8], urchin-like structures [9], disks [10] and tetrahedrons [10].

In the present contribution, the formation of submicron α-Fe_2O_3 cubes through oriented attachment of nanocrystal building blocks in acid iron (III) solutions at 100°C has been investigated in detail. In concrete, the growth mechanism of these structures was studied analyzing samples collected at different stages of the particle formation by various analytic techniques, such as X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Selected Area Electron Diffraction (SAED). In addition, vibrating sample magnetometry measurements were employed to examine the magnetic behaviors of the samples. These studies disclosed that the formation mechanism of the α-Fe_2O_3 cubes consists of several proposed growth mechanisms. Firstly, ultra-fine akaganéite particles are formed. Then, they grow to form akaganéite rod-shape particles that tend to aggregate into rather cubic structures. Finally, these rods experience a crystallo-chemical transformation to α-Fe_2O_3 and readjust their positions to form submicron polycrystalline cubes with pseudo-monocrystalline characteristics. Figures 1a-c show TEM micrographs of samples obtained at different reaction times. Figure 1d is the SAED pattern of an isolated submicron α-Fe_2O_3 cube. In agreement with this particle formation mechanism and their grainy structure, the submicron cubes exhibit magnetic properties mainly governed by surface effects. Particularly, the spin frustration of the antiferromagnetic coupling at nanocrystal surface give rise to exchange bias phenomena, suppression of the Morin transition and large coercivities at low and room temperature.

References

[1] C. A. Chen, Y.-M. Chen, Y.-S. Huang, D.-S. Tsai , K.-K. Tiong and P.-C. Liao, CrystEngComn **11** (2009) 2313.

[2] Z. Zhang, H. Sun, X. Shao, D. Li, H. Yu and M. Han, Adv. Mater. **17** (2005) 42.

[3] R. Mendoza-Reséndez, C. Luna, E. D. Barriga-Castro, P. Bombille and C. J. Serna, Nanotechnology **23** (2012) 225601

[4] P. D. Cozzoli, M. L. Curri, A. Agostiano, G. Leo and M. Lomascolo, J. Phys. Chem. B, **107** (2003) 4756.

[5] Z. Yu, M. A. Hahn, S. E. Maccagnano-Zacher, J. Calcines, T. D. Krauss, E. S. Alldredge and J. Silcox, ACS Nano **2** (2008) 1179.

[6] K.-S. Cho, D. V. Talapin, W. Gaschler and C. B. Murray, J. Am. Chem. Soc. **127** (2005) 7140.

[7] B. Jia and L. Gao, Crystal Growth & Design. **8** (2008) 1372.

[8] S. Zeng, K. Tang, T. Li, Z. Liang, D. Wang, Y. Wang and W. Zhou, J. Phys. Chem. C **111** (2007) 10217.

[9] S. Zeng, K. Tang,T. Li and Z. Liang J. Phys. Chem. C **114** (2010) 274.

[10] W. Wang, J. Y. Howe and B. Gu, J. Phys. Chem. C **112** (2008) 9203.

Figures

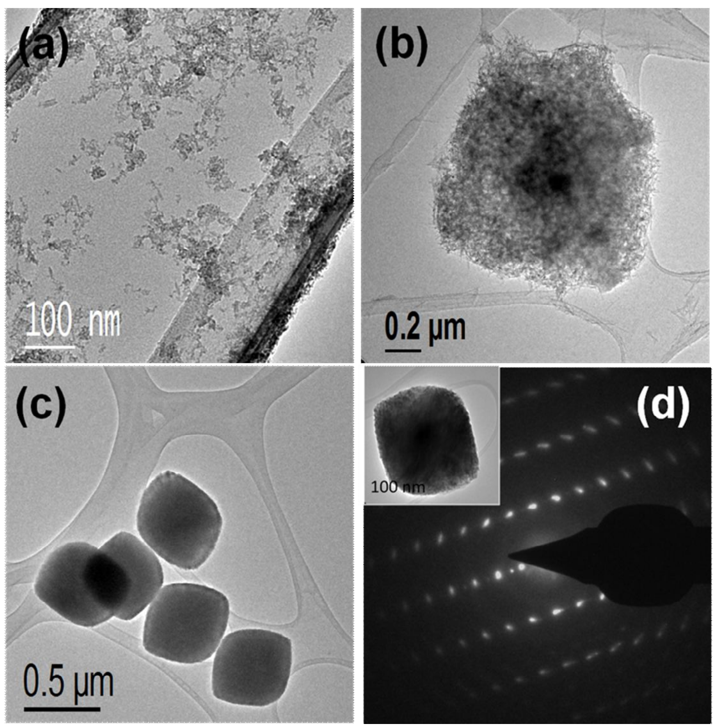

Figure 1. TEM images of the samples synthesized at a) 0, b) 4 and c) 24 hours. Part d) of the figure shows the SAED pattern of an isolated α-Fe_2O_3 cube.