

Electronic Supplementary Information to an article:

‘Controlled way to prepare quasi-1D nanostructures with complex chemical composition in porous anodic alumina’

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Section S1. Preparation and characterization of colloidal solutions of SrFe_{12-x}Al_xO₁₉ particles

Strontium hexaferrite nanoparticles were prepared via glass crystallization route.¹⁻² The composition of the initial glass corresponded to 8NaO_{0.5}-9SrO-11FeO_{1.5}-9AlO_{1.5}-8BO_{1.5}. The starting compounds (SrCO₃, Fe₂O₃, Al₂O₃, B₂O₃ and NaHCO₃, all chemical grade) were mixed in the respective ratios and melted for 2 h at 1250 °C in a platinum crucible. Then the melt was quenched between two rotating steel rollers to obtain a glassy material. Next, the glass was annealed at 700 °C or 750 °C for 2 h. During this procedure, glass ceramics containing hexaferrite nanoparticles were formed. To extract these particles the glass ceramics were treated with a 3 % solution of hydrochloric acid. Sedimentation of the magnetic phase was enhanced using a Nd-Fe-B magnet, and the supernatant solution was removed by decantation. The obtained precipitate was ultrasonically dispersed in water. Remaining large particles and aggregates were magnetically separated. The resulting transparent pale yellow-brown colloidal solution with pH value close to 5 had a hexaferrite concentration of order 0.01 vol. %. The samples were labeled as “solution 1” (obtained from the glass annealed at 700 °C) and “solution 2” (obtained from the glass annealed at 750 °C).

XRD pattern of the hexaferrite nanoparticles obtained from the solution 1 is presented in Fig. S1a. A considerable broadening of diffraction peaks is observed, and FWHM of (*hk*0) peaks is lower than FWHM of (*hkl*) peaks. This supposes the anisotropic shape of the nanoparticles with a much lower size in the *c* direction than in *a* and *b* directions. The XRD profile refinement (Rietan-2000) gave the lattice parameters *a* = 5.866(4) Å, *c* = 22.952(9) Å, and the crystallite size of 50 nm for *a*(*b*) and 7 nm for *c* direction, respectively. The lattice parameters are lower than typical parameters reported for SrFe₁₂O₁₉ (e.g. PDF 84-1531), apparently due to partial substitution of Fe for Al. By the Vegard's law, the estimated Al content amounts to *x* = 1.22 which agrees with EDX data.

Transmission electron microscopy confirmed platelet shape of the hexaferrite particles (Fig. S1b) with average thickness of 5 nm and average diameter of 60 nm. Selected area electron diffraction pattern recorded for a single particle (Fig. S1c) revealed monocrystallinity and hexagonal symmetry of the particle. The DLS size distribution profile for the colloidal solution 1 has a single peak which implies the average hydrodynamic diameter equals to 60 nm (Fig. S2). This suggests that the colloidal solution contained mostly non-aggregated single crystalline particles. The value of zeta-potential of the colloids was about 45 mV, which corresponds to stable dispersions.

TEM images show that the hexaferrite nanoparticles obtained from the solution 2 had similar platelet shape with an average thickness of 7 nm and an average diameter of 90 nm.

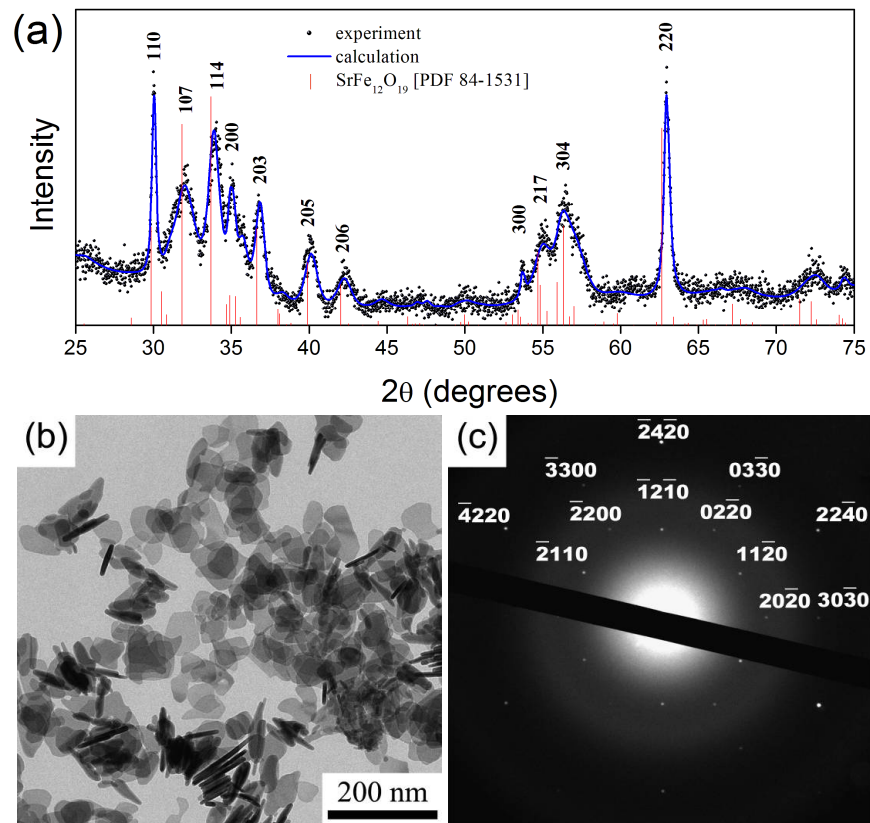


Fig. S1 (a) XRD data of the $\text{SrFe}_{12-x}\text{Al}_x\text{O}_{19}$ powder obtained from the dried colloidal solution. (b) TEM image of the particles. (c) Single particle electron diffraction pattern (electron beam is normal to the particle basal plane).

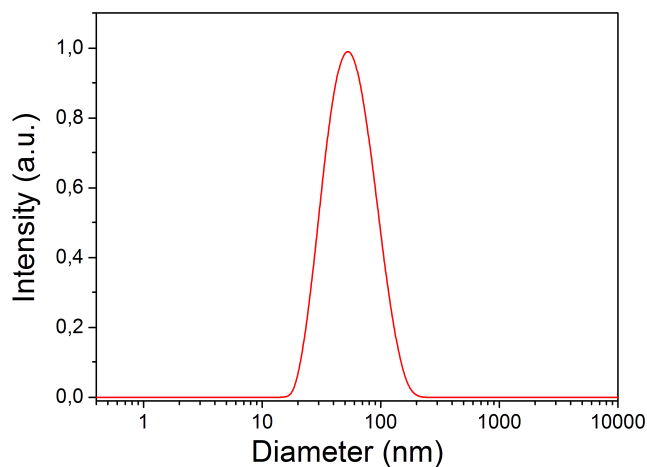


Fig. S2 Intensity distribution of hydrodynamic diameters of colloidal particles (DLS).

Section S2. Anodic aluminum oxide membranes.

High purity aluminum foils (99.999%, 0.5 mm thick, Goodfellow) were used as a starting material. Prior to anodization aluminum was annealed at 500 °C in air to remove mechanical stresses and to increase the grain size. Subsequently, the foils were mechanically polished to a mirror finish and cleaned repeatedly with acetone and deionized water. Anodization of aluminum was carried out in a two-electrode cell in 0.3 M $(\text{COOH})_2$ + 3 M $\text{C}_2\text{H}_5\text{OH}$ solution using platinum wire as a counter electrode. Voltage was kept at 40 V for 10 min and then was increased to the target voltage of 150 V with a constant rate of 1 V s^{-1} . The electrolyte was pumped through the cell and its temperature was kept at $-7 \text{ }^\circ\text{C}$. As the diameter of the pores and interpore distance depend on the applied voltage during anodization, in order to obtain 'blocking layer' voltage was decreased from 150 V to 75 V for 1 h.

To separate the porous oxide film from aluminum, the latter was dissolved in 10 vol. % Br_2 methanolic solution at room temperature. Subsequently, the dissolution of the barrier layer and etching of pores were carried out in a 5 vol. % H_3PO_4 aqueous solution at $60 \text{ }^\circ\text{C}$ for 20 min.

The anodic alumina membranes possessed uniform pores aligned at perpendicular to the film surface (Fig. S3). The channels formed a honeycomb-like structure with average interpore distance of 330 nm, which is typical for the applied anodization conditions.³ Average pore diameter of the synthesized AAO films was equal to 210 nm. SEM image of the alumina film chip confirms formation of the layer with the smaller diameter of the pores.

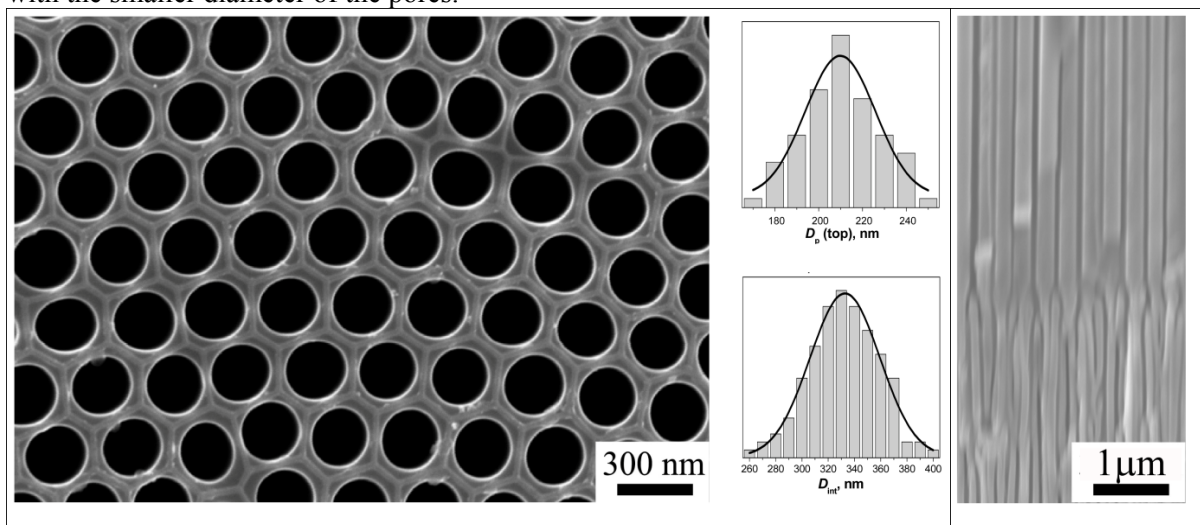


Fig. S3 Top view of AAO membrane (left) and distributions of pore diameter D_p and interpore distance D_{int} (right). The chip of the AAO membrane with 'blocking layer'.

Section S3. Sample characterization

The colloidal solutions were characterized by the dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Instruments) with backscattering configuration, correlation data were fitted using the DTS software package. Powder X-ray diffraction of hexaferrite nanoparticles was carried out on a Rigaku D/MAX 2500 diffractometer (40 kV, 120 mA, $\text{CuK}\alpha_1$ radiation, 2θ scan step 0.02°). High resolution scanning electron microscopy was performed using a SEM LEO Supra 50 VP with a micro-analytical system INCA Energy+ (EDX) Oxford. The magnetic properties of the samples prepared were studied with Quantum Design and Cryogenic S700 SQUID magnetometers at room temperature. Transmission electron microscopy was performed on a LEO 912 AB Omega.

References

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