Zig-zag Self-assembly of Magnetic Octahedral Fe₃O₄ Nanocrystals using in situ Liquid Transmission Electron Microscopy

Arnaud Demoitiere¹,²,³, Charudatta Phatak⁵, Andras Kovacs⁶, Jan Caron⁶, Nikita Repnin⁴, Martial Duchamp⁶, Nestor J. Zaluzec¹, Petr Kral⁴, Igor S. Aranson³, Rafal Dunin-Borkowski⁶, Alexey Snezhko³ and Dean Miller¹

¹. Electron Microscopy Center, Argonne National Lab, 9700 S Cass Av., Argonne, IL 60439, USA.
². Réseau pour le Stockage Electrochimique de l’Energie (RS2E) & Laboratoire de Reactivité et Chimie des Solides (LRCS), CNRS, UMR7314-UPJV, 33 Rue Saint Leu 80039 Amiens, France.
³. Materials science division, Argonne National Lab, 9700 S Cass Av., Argonne, IL 60439, USA.
⁴. Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60607, United States.
⁵. Nanoscience and Technology Division, Argonne National Lab, 9700 S Cass Av., IL 60439, USA.
⁶. Ernst Ruska Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Juelich GmbH, 52425 Juelich, Germany.

Direct imaging of colloidal nanoparticle solution by liquid phase transmission electron microscopy [1] enables unique in situ study of nanocrystal self-organization [2] and offers a great opportunity to improve understanding of fundamental mechanisms governing self-assembly at nano-scale. In equilibrium, different aspects of self-assembly can be described in term of thermodynamics of interacting particles. However, out of equilibrium, long-range hydrodynamic interactions play also an important role in the process and expected to become more significant, for instance, in charged solvent media with electrophoresis effect. Real time/nanoscale capable instrumentation is needed for the successful design of large-scale particles arrays suitable for effective device architectures. Since the size domain of nanoparticle self-assembled lattices is below the diffraction limit of visible light, the X-ray scattering techniques, such as SAXS and GISAXS have been used as being the best tool in the study of the superlattice growth (in situ or ex situ) at liquid/air and liquid/substrate interfaces. However, nanoscopic details remain elusive during the super-cluster formation, such as particle dynamics, surface re-building, re-arrangement effect, and relative position. The latest developments in liquid cell TEM technology opens up a new window for in situ study at nanoscale.

The goal of our project is to investigate the self-assembly of magnetic nanocrystals in solution at nanoscale using liquid TEM setup. The liquid-cell microchip (Protochips – Poseidon 200) [3] is consisted of a hermetically sealed liquid-filled chamber (thickness from 0.5 to 2 μm) sandwiched between two silicon nitride membranes. The liquid cell experiments enable direct imaging of phenomena occurring during the self-assembly process. We were able to induce self-assembly of magnetic octahedral nanocrystals in liquid cell inside TEM (Tecnai F20ST – EMCAngonne NL) using Lorentz lens (and mini-lens) with which a magnetic field (0.1 to 2T) can be applied (parallel to e-beam). Chains of Fe₃O₄ nanocrystals are then formed inside the liquid cell along of the magnetic field. The octahedral nanocrystals are assembled in chain with a zig-zag configuration due to the orientation of magnetic easy axis (perpendicular to {111} facets). We studied self-organization behaviors as a function of applied magnetic field, type of solvent and liquid cell spacer. To the best of our knowledge, this is the first example of self-assembly control of magnetic nanocrystals inside TEM in liquid medium. This novel tool will provide unique capabilities to tackle fundamental problems of colloidal dynamics and self-assembly, for instance, by precise quantization of driving forces at nanometer scale. Monte-Carlo simulations were used to understand processes of the formation of these complex nano-chains consisted
of octahedral particles (figure 1). Finally, as shown in the figure 2, Lorentz microscopy and the electron holography were used to study the magnetic induction within and around a chain of magnetite nanocrystals formed during the in situ liquid cell experiment [4].


Figure 1. (a) Zig-zag chain of magnetic octahedral Fe₃O₄ nanocrystals aligned within liquid cell TEM under magnetic field applied using Lorentz lens. Inset Monte-Carlo simulation of chain assembly under magnetic field (b) Scheme of octahedra aligned in zig-zag chain. (c) Liquid in situ TEM picture of chain of Fe₃O₄ nanocrystals. (d) Sketch of octahedral with magnetic easy axis [111].

Figure 2. Magnetization map of a Fe₃O₄ nano-chain obtained using Lorentz microscopy. Magnetic induction map (electron holography) of a chain of particles with three crystals. The contour spacing is 0.25 rad. The color code represents the direction of the projected magnetic induction. Bright-field TEM image of the same chain is shown in insert. The scale bars are 50 nm.