

Characterizing the calcination behaviours of Ni-Fe layered double hydroxide materials via in-situ transmission electron microscopy

Hobbs, C.¹, Jaskaniec, S.², McCarthy, E.K.³, Downing, C.³ and Nicolosi, V.⁴

¹ School of Physics and CRANN, Trinity College Dublin., Ireland, ² School of Chemistry and AMBER, Trinity College Dublin, Dublin, Ireland., Ireland, ³ The Advanced Microscopy Laboratory, CRANN, Trinity College Dublin., Ireland, ⁴ School of Chemistry and AMBER, Trinity College Dublin., Ireland

Layered double hydroxides (LDHs), a member of the two-dimensional nanomaterial category, are considered as versatile materials due to broad applications in medicine¹, catalysis² and flame retardants³. Moreover, LDHs have been extensively utilized as precursor materials for catalytic applications where the calcination of the precursor layered materials results in the generation of catalytically active materials having applications in photocatalysis⁴, hydrogen production⁵ and magnetic materials⁶. However, a detailed description and observation of the nanoscale thermal evolution mechanisms has yet to be revealed. Herein, we report an *in-situ* transmission electron microscopy (TEM) characterization of Ni-Fe LDHs, revealing the nanoscale mechanisms involved with the thermal evolution of these versatile nanomaterials⁷.

The precursor LDH platelets were first characterized by TEM (FEI Titan, Oregon, USA) and selected area electron diffraction (SAED) before subject to heated environments via an *in-situ* heating TEM sample holder (DENS Solutions, The Netherlands). Subsequently, the properties of the calcined samples were post-analyzed in the TEM *via* energy filtered TEM (EFTEM), as well as energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) using scanning TEM (STEM).

Figure 1 presents bright field TEM images and corresponding selected area electron diffraction (SAED) patterns from various stages of *in-situ* heating experiments. Initially the Ni-Fe LDH material was found to have a hexagonal morphology with a well-defined crystal structure of hexagonal symmetry, typical of an LDH material (Figure 1(a)). As the platelets were subject to the incremental heating ramp, both a morphological and crystallographic transformation occurred. At 450°C, the LDH material appeared to have an altered morphology, with a nucleation of spherical nanoparticles on the platelet surface (Figure 1(b)). Moreover, SAED analysis at this temperature indicated a loss of certain reciprocal lattice vectors, indicating a transition towards an amorphous phase. At 850°C, the LDH materials thermally evolved into a confined array of spherical nanoparticles as a result of further nucleation, along with a change in crystallographic structure (Figure 1 (c) and (f)). Post-analysis of the calcined material showed that these spherical particles were predominantly composed of Nickel, as shown by EDX mapping in STEM (Figure 2 (c)). Also, these spherical particles were surrounded by Iron containing materials, highlighted by EELS mapping of the Iron L₃ edge (Figure 2(d)).

The application of *in-situ* transmission electron microscopy revealed the nanoscale mechanisms involved in the thermal evolution of Ni-Fe LDH nanomaterials. The LDH precursor platelets were found to evolve into an array of coexisting Ni-containing oxide particles amongst an Iron-containing spinel matrix, confirmed by SAED, EFTEM as well as STEM-EDX and STEM-EELS mapping techniques.

- (1) Rives, V.; Arco, M.; Martín, C. Layered Double Hydroxides as Drug Carriers and for Controlled Release of Non-Steroidal Antiinflammatory Drugs (NSAIDs): A Review. *J. Control. Release* **2013**, *169*, 28 - 39.
- (2) Xu, Z. P.; Zhang, J.; Adebajo, M. O.; Zhang, H.; Zhou, C. Catalytic Applications of Layered Double Hydroxides and Derivatives. *Appl. Clay Sci.* **2011**, *53*, 139 - 150.
- (3) Gao, Y.; Wu, J.; Wang, Q.; Wilkie, A.; Hare, D. O. Flame Retardant Polymer / Layered Double Hydroxide Nanocomposites. *J. Mater.* **2014**, *2*, 10996 - 11016.
- (4) Yuan, X.; Jing, Q.; Chen, J.; Li, L. Photocatalytic Cr(VI) Reduction by Mixed Metal Oxide Derived from ZnAl Layered Double Hydroxide. *Appl. Clay Sci.* **2017**, *143*, 168 - 174.
- (5) Abellò, S.; Bolshak, E.; Montané, D. Ni - Fe Catalysts Derived from Hydrotalcite-like Precursors for Hydrogen Production by Ethanol Steam Reforming. *Appl. Catal. A Gen.* **2013**, *450*, 261 - 274.

- (6) Zhou, T.; Feng, L.; Zhan, K.-T.; Evans, D. .; Duan, X.; Zhang, M.-L. Preparation and Characterization of Layered Precursor Nickel - Iron Hydrotalcites and Magnetic Materials. *Acta Chim. Sin.* **2002**, *60*, 1078 - 1083.
- (7) **Hobbs, C.**; Jaskaniec, S.; Mccarthy, E. K.; Downing, C.; Opelt, K.; Güth, K.; Shmeliov, A.; Mourad, M. C. D.; Mandel, K.; Nicolosi, V. Structural Transformation of Layered Double Hydroxides": An in Situ TEM Analysis. *npj 2D Mater. Appl.* **2018**, *2*.

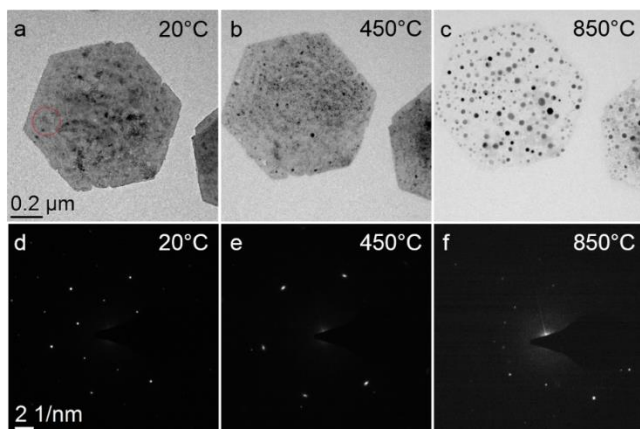


Figure 1. (a)-(c) Bright field TEM images and corresponding (d)-(f) selected area electron diffraction patterns from various steps of the *in-situ* heating of the Ni-Fe LDH nanomaterial. Red circle in (a) indicates acquisition region of associated electron diffraction patterns.

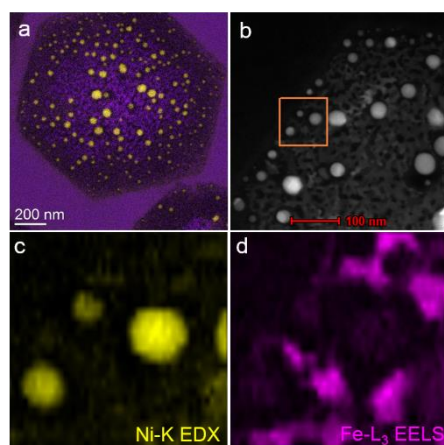


Figure 2. (a) Composite Ni (yellow) and Fe (purple) EFTEM maps of the calcined LDH platelet. (b) STEM image of calcined LDH material. Orange square indicates STEM-EDX/STEM-EELS map acquisition area. (c) Ni-K EDX map. (d) Fe-L₃ EELS map.

The authors would like to thank the Advanced Microscopy Laboratory, Trinity College Dublin, Ireland for provision of their facilities. The funding agencies, SFI AMBER, SFI PIYRA, ERC StG 2D NanoCaps, ERC CoG 3D2DPrint and Horizon2020 NMP Co-Pilot are also thanked for their support.