Visualizing the Growth of LDH Nanomaterial through Electrodeposition and Chemical Conversion

Wenhui Wang[1, 2], Hongwei Yan[1, 2], Ivan Erofeev[1, 2] and Utkur Mirsaidov[1, 2, 3, 4]

[1] Centre for BioImaging Sciences, Department of Biological Sciences, National University of Singapore, Singapore.
[2] Department of Physics, National University of Singapore, Singapore.
[3] Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, Singapore.
[4] Department of Materials Science and Engineering, National University of Singapore, Singapore.

A shift towards environment-friendly economy based on renewable energy sources requires cost-efficient, highly active and stable electrocatalysts to facilitate various energy conversion reactions. Transition metal layered double hydroxides (LDH) are attractive materials for these catalysts because of their high-surface-area 2D layered structure, compositional diversity, structural stability and earth abundance [1]. LDHs are a class of inorganic lamellar compounds composed of layers of bivalent and trivalent metallic cations with charge compensating anions occupying the interlayer regions [2]. LDH nanomaterial are normally synthesized via either of two approaches: direct synthesis [3] featuring co-deposition, hydrothermal reaction or electrodeposition, and chemical conversion [4], for example, from MOF nanoparticles through chemical etching. Despite significant advances in the synthesis of high-performance and durable LDH-based electrocatalysts, the underlying details of the growth process of LDH materials are still unknown. The most appealing approach to capturing the dynamics of LDH formation and clarifying the related mechanisms is a direct visualization of these nanoscale processes as they take place, which can only be achieved with *in situ* electron microscopy observations.

Here, we demonstrate the advantage of using *in situ* liquid cell TEM to directly observe the growth of LDH nanomaterials with high temporal and spatial resolution. We study direct electrochemical deposition of LDH with *in situ* electrochemical liquid cell, exploring a range of precursor solution concentrations and deposition potentials. Real time observation allows us to follow the development of radically different morphologies of deposited LDH nanosheets upon varying the precursor concentration [5], as shown in Figure 1. In another study we pursued the goal to obtain hollow LDH nanostructures via chemical conversion reactions. We adopt liquid-phase TEM imaging to resolve the details of how ZIF-8 NP templates are converted into hollow LDH nanocages, see Figure 2. We show that LDH nanosheets nucleate and grow on the surface of template ZIF-8 NP, whereas the ZIF-8 NP itself is gradually etched, and so the formation of well-defined LDH nanocages requires a subtle balance between the etching and growth rates [6].

References:

[1] Q Wang, D O'Hare, Chem. Rev. **112** (2012), p. 4124.
[2] J Yu *et al*, Chem. Soc. Rev. **46** (2017)**,** p. 5950.
[3] G Chen *et al*, Adv. Energy Mater. **10** (2020), p. 902535.
[4] D Liu *et al*, Adv. Mater. **31** (2019), p. 1803291.
[5] W Wang *et al*, Nano Lett. **21** (2021), p. 5977.
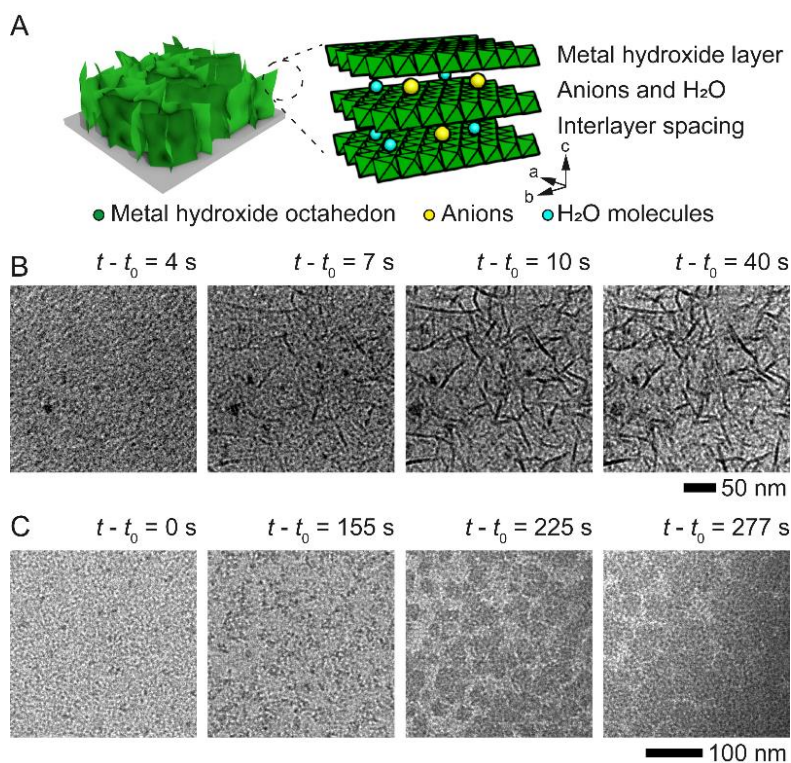[6] W Wang *et al*, Am. Chem. Soc. **143** (2021), p. 1854.

CrossMark

Figure 1. *In situ* electrodeposition of LDH nanosheets. (A) Schematic of LDH nanosheets on a working electrode. Time series of *in situ* TEM images showing the growth of vertical LDH nanosheets on the carbon-coated working electrode of a liquid cell biased at –0.6 V from an aqueous solution containing: (B) 150 mM $Co(NO_3)_2$ and 150 mM $FeSO_4$. (C) 15 mM $Co(NO_3)_2$ and 15 mM $FeSO_4$.
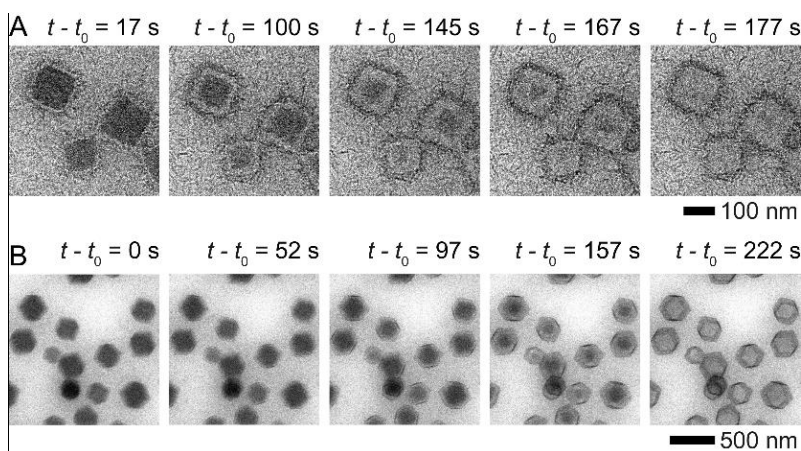

Figure 2. Conversion of ZIF-8 NPs into LDH nanocages in a $Co(NO_3)_2$ solution. Time series of *in situ* liquid-phase TEM images showing the room-temperature conversion of ZIF-8 NPs into LDH nanocages in a 5 mg mL^{-1} $Co(NO_3)_2$ solution with ethanol–water solvent ($V_{EtOH}/V_{H2O} = 0.5$): (A) ZIF-8 nanocubes, (B) ZIF-8 rhombic dodecahedron NP. Here, t_0 represents the time point corresponding to the onset of the etching (i.e., when the etching was first visually detected).