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Processing of Layered Double Hydroxides for Energy Applications

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Introduction

Layered double hydroxides (LDHs) are a class of anionic clays consisting of positive charged brucite-like layers spaced by water molecules and counterbalancing anions[1]. In particular, transition metals LDHs have drawn attention for energy storage and conversion applications[2] because of their electrocatalytic properties for water splitting[3], and pseudocapacitive behavior[4][5]. Contrarily to other layered materials, LDH layers are held together by electrostatic forces and a dense network of hydrogen bonds[6]. For these reasons, a careful choice of solvent is pivotal for an efficient exfoliation of the LDHs. One of the most effective is formamide[1][7]. However, due to formamide toxicity and its high boiling temperature, other solvent options are recommended for the processing of LDHs[8][9].

Synthesis

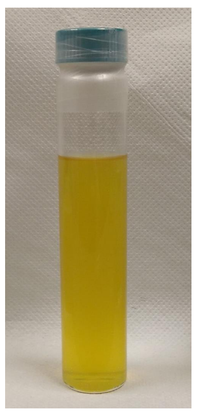


Figure 1. *A picture of the NiFe-LDH dispersion in ethanol.*

- Hydrothermal synthesis of NiFe-LDH from aqueous metal salts solution following the Jaśkaniec's method[10].
- Treatment of the obtained LDH with an acetate aqueous solution.
- Multiple extractions from treated LDH, using ethanol as extracting solvent, lead to a yellow dispersion (Figure 1).

Hexagonal nanoplatelets

Dispersed particles are hexagonal nanoplatelets about 200 nm wide (Figure 2) showing partial exfoliation (Figure 4). X-ray diffraction pattern shows that thin films obtained from the NiFe-LDH nanoplatelets dispersion have an high isotropic orientation (Figure 3).

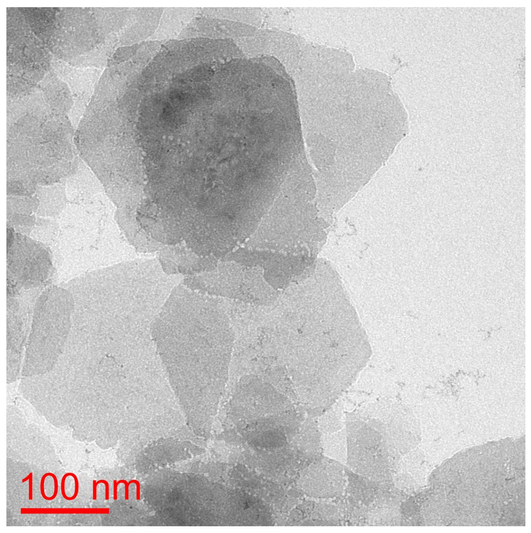


Figure 2. *Transmission electron microscopy image of hexagonal NiFe-LDH nanoplatelets.*

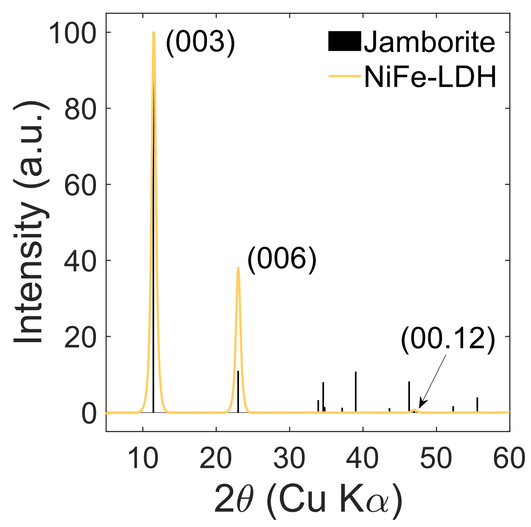
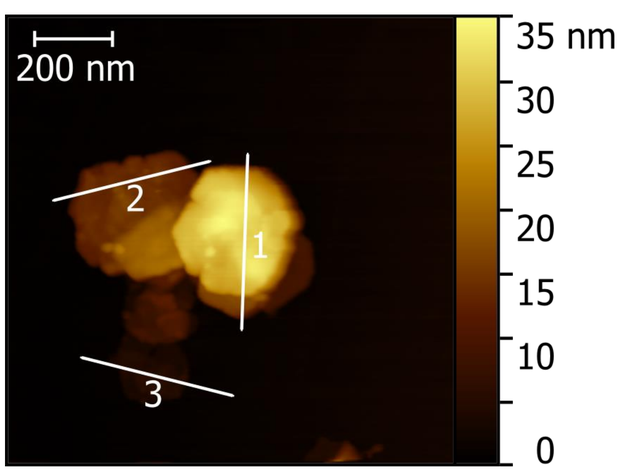


Figure 3. *X-ray diffraction pattern of NiFe-LDH spay coated on Si.*



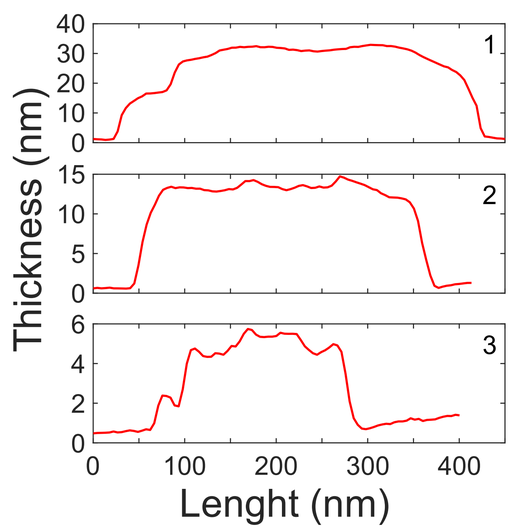


Figure 4. *Atomic force microscopy image (left) and profiles (right) of partially exfoliated nanoplatelets.*

Investigation on the dispersion mechanism

The acetate ion has been revealed to be present alongside with the LDH by comparing ultraviolet-visible light (UV-Vis) spectra of the LDH dispersion and a sodium acetate solution (Figure 5), while UV-Vis spectroscopy can be used to monitor the undergoing dispersion process (Figures 6,7).

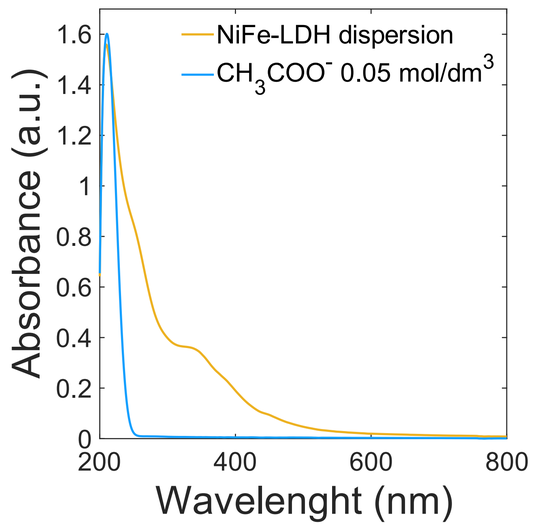


Figure 5. *Comparison between UV-Vis spectra of the LDH dispersion and a sodium acetate solution in ethanol.*

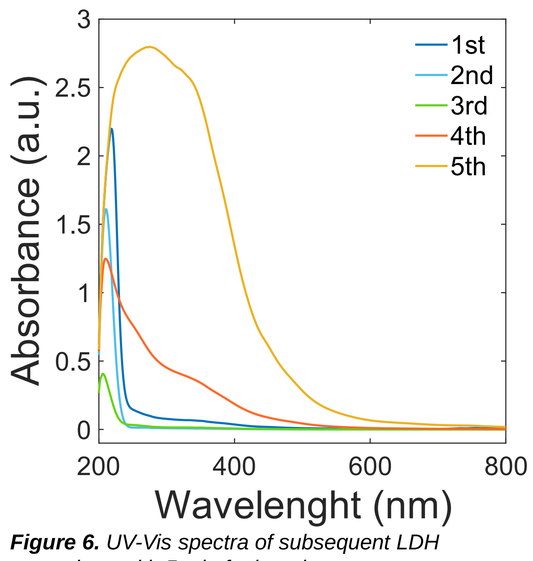


Figure 6. *UV-Vis spectra of subsequent LDH extractions with 5 ml of ethanol.*

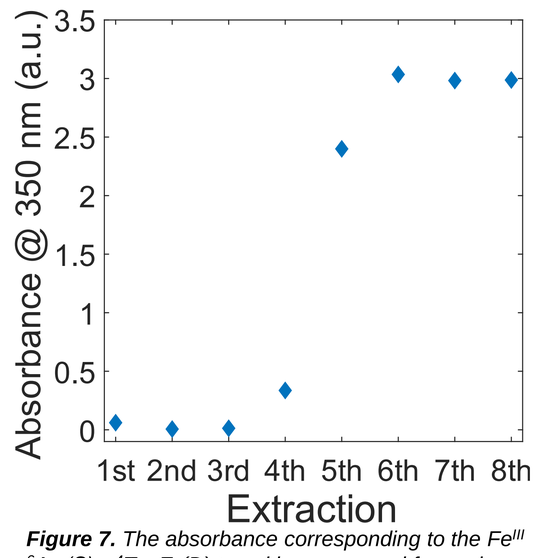


Figure 7. *The absorbance corresponding to the Fe^{III} $^6A_{1g}(S)\rightarrow{}^4T_{2g},E_g(D)$ transition measured for each extraction.*

Electrochemical Characterization

Graphite paper electrodes spray-coated with LDH dispersion show promising electrocatalytic properties to the oxygen evolution reaction.

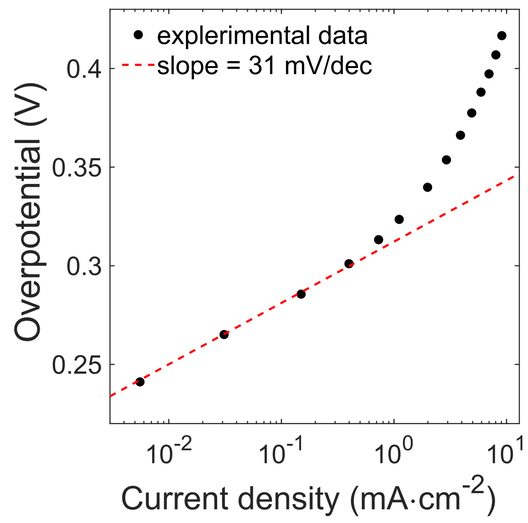


Figure 8. *Polarization curve measured on LDH@graphite paper electrode in KOH 0.1 mol/dm³ aqueous solution.*

Overpotential at 10 mA/cm²: 340 mV.

Electrode resistance: 38 Ω.

Tafel slope of 31 mV/dec (Figure 8) with an exchange current of $8.9\cdot10^{-11}$ A/cm².

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