Charles University
Faculty of Science

Study programme: Inorganic Chemistry

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Layered Transition Metal Hydroxides: Delamination and Properties

Extended abstract

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Layered transition-metal hydroxides have attracted increasing attention as promising active electrode materials for electrochemical energy storage and conversion device due to facile preparation and modification, good tunability, high capacitance capability, fast reversible redox reactions, and cost effectiveness. Many reported hierarchical architectures based on nickel and cobalt hydroxides are composed of bulky nanoplatelet-like aggregates; however, the nanomorphology and behavior of the separated hydroxide nanosheets is much less known.

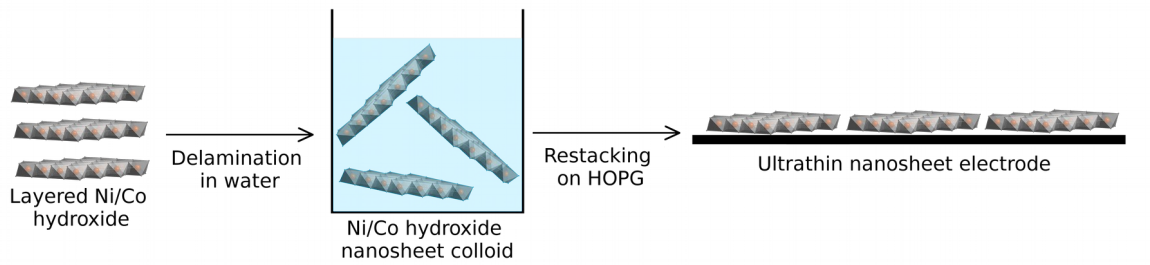

Figure 1. Scheme of layered nickel or cobalt hydroxide delamination and subsequent restacking on conductive HOPG support.

In this respect, the dissertation thesis reports characterization and electrochemical performance of nickel, nickel-cobalt, and cobalt hydroxide nanosheets, synthesized by an economical and environmentally friendly method based on delamination of corresponding layered hydroxides in water (Figure 1). For this purpose, lactate and nitrate layered hydroxides were prepared by two synthetic procedures, leading to desired materials: alkaline precipitation (Equation 1) and anion exchange reaction (Equation 2) from dodecyl sulphate layered hydroxide precursor. The products differed in composition and properties according to the preparation method used, as evidenced by powder XRD, IR and UV-Vis spectroscopy, thermal and elemental analyses.

$$2M(A^-)_2 + 3NaOH \rightarrow M_2(OH)_3A^- + 3NaA^- \quad (1)$$

$$M_2(OH)_3DS + NaA^- + CTABr \rightarrow M_2(OH)_3A^- + CTA\text{-}DS + NaBr \quad (2)$$

($M = Ni^{2+}, Co^{2+}$, $A^- = Lac^-, NO_3^-$, DS = dodecylsulphate anion, CTABr = hexadecylammonium bromide)

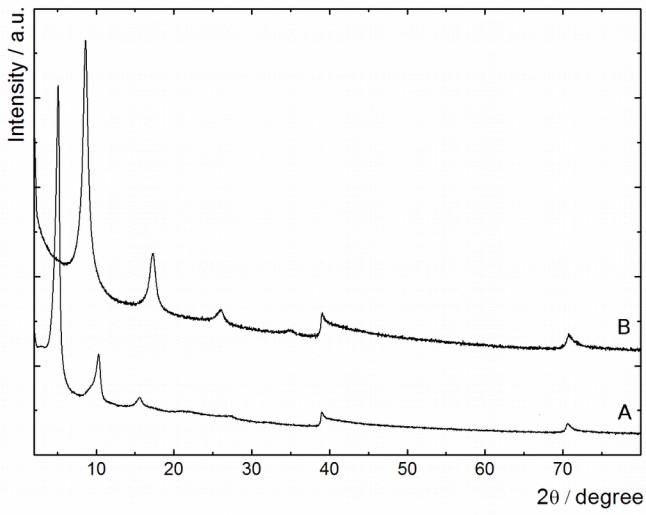

Figure 2. XRD patterns of prepared layered cobalt hydroxides; dodecyl sulphate intercalated precursor (A) and layered cobalt hydroxide lactate (B). Shift of basal diffraction maxima is caused contraction of interlayer distance evidencing successful anion exchange. The curves are vertically shifted for better clarity.

The hydroxide nanosheets were prepared by delamination of corresponding layered hydroxide lactates or nitrates in water and formed transparent colloids that were stable for months (Figure 3.A). In all cases, the delamination was well reproducible and practically quantitative. The nanosheet concentrations were up to 30 mg mL^{-1}. At higher concentrations, the dispersions formed gels. The morphology of the hydroxide nanosheets was investigated by small angle X-ray scattering method (SAXS), AFM, and TEM. The combination of SAXS, characterizing directly colloidal dispersions, with microscopy analyses of nanosheet deposits evidenced the presence of the single hydroxide hexagonal nanosheets of approximately 1 nm thickness. Lateral dimension was between 50 and 80 nm. (Figure 3.C).

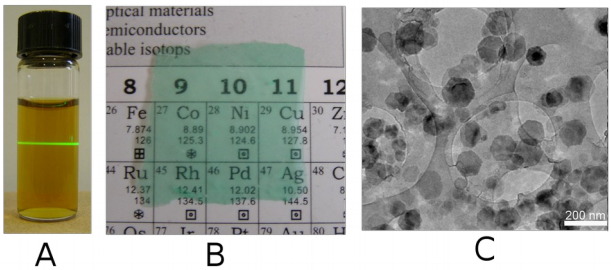

Figure 3. Cobalt hydroxide nanosheet colloid (A), nickel hydroxide nanosheets self-standing film (B), TEM Image of hexagonal-shaped nickel hydroxide nanosheets (C).

The resulting colloids were used for the fabrication of ultrathin electrodes composed of restacked nanosheets. The drop-casting method lead to thicker films with the preference

orientation of the nanosheets (Figure 3.B) as was documented by XRD reflection and transmission experiments (Figure 4). The nanometric hydroxide ultrathin films were prepared by spin-coating method.

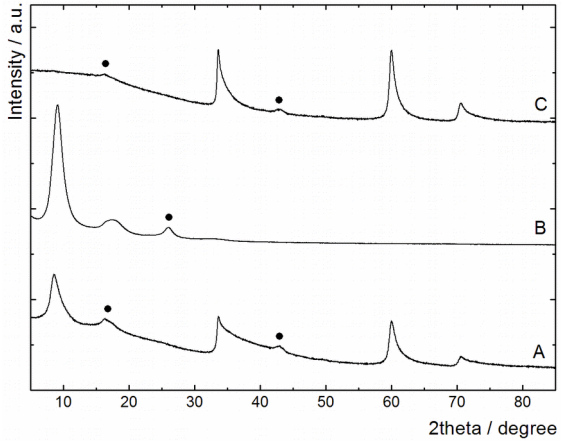

Figure 4. Powder XRD patterns of layered nickel hydroxide oriented film documenting the preferential orientation of nickel hydroxide nanosheets; basal diffractions are visible only in reflection mode (B) whereas nonbasal diffractions are visible in transmission mode (C). Diffraction pattern of powder sample with random nanosheet orientation in transmission mode is displayed for comparison (A). Mylar foil support is labelled (●). The curves are vertically shifted for better clarity.

The deposition of the nanosheets allowed an investigation of electrochemical behaviour of the nickel, cobalt, and nickel-cobalt hydroxide nanosheets not affected by bulk effects. The voltammetric curves of deposited nanosheets showed different behavior than that of corresponding thicker films. The study indicates that Co-doping in mixed nickel-cobalt hydroxide nanosheets improved the performance of the nanosheets by decreasing the time of their electrochemical activation, which for the pure nickel hydroxide nanosheets requires much more potential sweeps. Thanks to the nanometric thickness, the ultrathin electrodes showed very fast electrochemical response in the comparison with the conventional bulky nickel and cobalt hydroxide electrodes. The nanosheets prepared by the present method show promise for use in nanocomposite materials for energy storage applications.