Supporting Information

Ni³⁺ doped monolayer layered double hydroxide nanosheets as efficient electrodes for supercapacitors

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Part S1. Experimental sections

Materials

Chemicals. Ni(NO₃)₂·6H₂O, TiCl₄, Al(NO₃)₃·6H₂O, urea, sodium dodecyl sulfate (SDS) and isooctane were purchased from Sigma-Aldrich Co.

Synthesis of LDHs:

Monolayer-NiTi-LDH nanosheets were synthesized using a reverse microemulsion method firstly reported in our previous work.^[1] Typically, 1.1 mL of water, 50 mL of isooctane and 1.80 g of SDS were mixed to form a transparent reverse emulsion system with the assistance of co-surfactant 1-butanol (1.5 mL). Then, 0.004 mol of Ni(NO₃)₂·6H₂O, 0.001 mol of TiCl₄ and 1.2 g of urea were added and aged at 110 °C for 27 h in an oil bath. Finally, the precipitates were separated.^[1b] It is noted that by controlling the amount of SDS, the particle sizes of products can be easily adjusted.

For comparison, bulk-NiTi-LDH^[1b] and bulk-NiAl-LDH^[2] were also prepared according to the literature.

Characterization. XRD patterns were collected using Bruker DAVINCI D8 ADVANCE diffractometer. The morphology of the samples was characterized by JEOL-2100F transmission electron microscope. FTIR spectra were recorded using Perkin Elmer GX spectrophotometer. The size and thickness of LDH nanosheets were determined by AFM (Multimode Nanoscope IIIa, Veeco Instruments). Brunauer-Emmett-Teller (BET) surface areas and pore-size distributions were tested using a Quantachrome Autosorb-1C-VP apparatus at 77 K. XPS spectra were obtained by PHIQ2000 X-ray photoelectron spectrometer, and the binding energy is calibrated with C1s = 284.8 eV. EPR spectra were collected on a JES-FA200 at 110K.

Electrochemical tests. The electrochemical measurements were carried out with a CHI 660B using a three-electrode cell with a platinum foil, a saturated Ag/AgCl electrode and a Ni foam electrode coated with LDHs. The CV curves were recorded in de-aerated acetonitrile with

KOH (1 mol L^{-1}) as the electrolyte. The EIS measurements were tested in the frequency range of 0.01-10⁵ Hz.

The 1 cm \times 1 cm electrode was fabricated as follows: LDH samples (80 wt %), acetylene black (15 wt %) and poly (tetrauoroethylene) (PTFE) (5 wt %) were dispersed in ethanol to produce a homogeneous paste. For the delaminated monolayer LDH, the colloids without drying were used directly. The nickel foam was finally coated by the above slurry. The electrode was then pressed and dried.^[3] The mass of electrodes was ca. 2 mg.

The specific capacity incharge-discharge was derived from the following equation:

$$C = \frac{i\Delta t}{\mathrm{m}\Delta V}$$

where *m* represents the mass of eletrode material, ΔV is the voltage change after discharge process, *i* refers to the discharge current during the electrochemical process and Δt represents the discharge time.

Calculation method. Plane-wave density functional theory calculations for the electronic property of bulk-NiTi-LDH and Ni³⁺ doped monolayer-NiTi-LDH with oxygen defect sites were carried out using Dmol3 module in Material Studio. The $3\times6\times1$ supercell was adopted for bulk-NiTi-LDH as initial structure with lattice parameters $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$, a = 15.735 Å, b = 6.294 Å. The parameter c was referred to the experimental data of this work (7.160 Å for bulk-NiTi-LDH). The generalized calculation details were the same as those in our previous report.^[1b] The calculation was performed at the "Chemical Grid Project" of Beijing University of Chemical Technology.

Part S2. Characterization of LDH samples



Scheme S1 Schematic illustration for the formation of bulk LDH particles in water: (A) the mixture of metal salts and urea in water; (B) urea undergos hydrolysis and LDH phase starts to crystallize; (C) LDH products with more stacking layers continue to crystallize and grow in aqueous solution; (D) the final LDH particles in aqueous solution after cleaning.



Fig. S1 TEM and HRTEM images of (A, B) bulk-NiTi-LDH, and (C, D) bulk-NiAl-LDH.



Fig. S2 XRD patterns of (a) bulk-NiAl-LDH, (b) bulk-NiTi-LDH and (c) monolayer-NiTi-LDH.



Fig. S3 FT-IR spectrum of monolayer-NiTi-LDH.



Fig. S4 Galvanostatic discharge curves for (A) monolayer-NiTi-LDH, (B) bulk-NiTi-LDH, and (C) bulk-NiAl-LDH at various discharge current densities.

Fig. S5 Cycling stability of (a) monolayer-NiTi-LDH, (b) bulk-NiTi-LDH and (c) bulk-NiAl-LDH.

Fig. S6 Local fine EPR spectra of monolayer-NiTi-LDH at 110 K under Ar atmosphere: around (A) 240-266 mT and (B) 305-335 mT.

Fig. S7 EPR spectra of (a) bulk-NiTi-LDH and (b) bulk-NiAl-LDH at 110 K under Ar atmosphere.

Fig. S8 Supercell model of (A) Ni³⁺ doped monolayer-NiTi-LDH with hydrogen vacancy (in yellow circles), and (B) bulk-NiTi-LDH with 3×6×1 rhombohedral lattice (Grey: Ti; Blue: Ni; Red: O; White: H).

Fig. S9 TDOS and PDOS of bulk-NiTi-LDH.

References

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