Supporting Information

Phase Engineering of Cobalt Hydroxides by Magnetic Fields for

Enhanced Supercapacitor Performance

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Experimental Section

Preparation of cobalt hydroxides. All chemicals are of analytical grade and used as received. In a typical synthesis, 0.48 g of CoCl₂·6H₂O and 0.3 g of PVP were dissolved in 20 ml distilled water. After being vigorously stirred for 15 minutes, 0.75 ml of hydrazine was dropwise added into the above mixture solution. Then the pink solution was divided into three pieces equally and transferred into three Telflon-lined stainless steel autoclaves with 60 ml capacity (the first one without external magnetic field, the second one with two NdFeB magnets under and on the Teflon vessel, respectively. The magnetic field strength on the inner surface of the Teflon vessel was 0.25 T at room temperature, 0.2 Tesla at reaction temperature of 180 °C. The third one was with applied magnetic field of 2 Tesla), respectively. All of the autoclaves were tightly to perform hydrothermal processes at at 180 °C for 8 h, and a schematic diagram of synthetic device under 2 T magnet can be seen in Figure S1. After the reaction was completed, the resulting powders were collected and rinsed with distilled water and alcohol three times, respectively. Then the products were dried in air at 50 °C for 4 h. The as-obtained samples showed different colors and were labeled as sample S_0 (pink particles), $S_{0.2T}$ (the mixture of pink and green particles) and S_{2T} (green particles), respectively, where 0, 0.2 Tesla and 2 Tesla indicated the strength of applying magnetic field.

Characterization of as-synthesized samples. The as-obtained samples were ground into powders for characterization. The phases, morphologies and microstructures were characterized by X-ray powder diffraction (XRD, Bruker D8-ADVANCE) using an 18 Kw advanced X-ray diffractometer with Cu Ka radiation (λ =1.54056 Å), Fourier transform infrared (FTIR) spectra (Nicolet FTIR Avatar 360 with KBr method), X-ray photoelectron spectroscopy (XPS, PHI-5702 instrument with Al K α radiation), scanning electron microscopy (FESEM, FEI Sirion 200) and high resolution transmission electron microscopy (HRTEM, JEOL-2010). The magnetic properties were investigated by a vibrating sample magnetometer (VSM, PMC MicroMag 3900) at room temperature equipped with 1T magnet. The electrochemical measurements were carried out on an electrochemical workstation (CHI 660E, Chenhua, Shanghai) with a three-electrode electrochemical cell containing 2M KOH aqueous solution as the electrolyte. The working electrode was made up of active material (Co(OH)₂/NiO, 85 wt%), conductive materials (acetylene carbon black, 10 wt%) and blinder (polyvinylidenedifluoride, PVDF, 5 wt%), and the active material was controlled to be at least 2 mg/cm². Platinum foil and saturated calomel electrode (SCE) acted as counter and reference electrode, respectively.



Figure S1. Schematic diagram of synthetic device in 2 T magnetic field.



Figure S2. XRD patterns of sample S_{S1} obtained using CoNO₃ precursor in the absence of magnetic field (a), S_{SM1} obtained using CoNO₃ precursor in the presence of 2T magnetic field (b), S_{S2} using CoSO₄ precursor in the absence of magnetic field

(c) and S_{SM2} using CoSO₄ precursor in the absence of magnetic field(d).



Figure S3. XRD patterns of cobalt hydroxides synthesized at different temperature under 0 T (a), and 2 T (b). Sample S_{S3} and S_{SM3} were prepared at 160 °C under 0 T and 2 T. Sample S_{S4} and S_{SM4} were obtained at 200 °C under 0 T and 2 T, respectively.



Figure S4. XPS spectra of sample S_0 and S_{2T} : (a) survey scan; (b) Co 2p; (c) Cl 2p; (d) O 1s.



Figure S5. EDS spectra of sample $S_0,\,S_{0.2T}$ and $S_{2T.}$



Figure S6. XRD patterns of cobalt hydroxides synthesized with different alkali sources under 0 T (a), and 2 T (b). Sample S_{S5} and S_{S6} were prepared with urea and ammonia under 0 T, respectively. S_{SM5} and S_{SM6} were synthesized with urea and ammonia under 2 T magnetic field, respectively.



Figure S7. Nitrogen physisorption isotherms of samples S_{0} , $S_{0.2T}$ and S_{2T} .



Figure S8. XRD (a) and EDS (b) patterns of sample S_{2T} and cycled S_{2T} (labeled S_C), and SEM image of sample S_{2T} (c) and S_C (d)

To examine the magnetic field effects on the synthesis of other droxide phase. Nickel hydroxide was chosen and NiCl₂ precursor was used with all other synthetic parameters kept unchanged. The results were presented in Figure S9. In the absence of a magnetic field during synthesis, the product (labeled as S_{S7}) was found to be metallic Ni nanopowders (JCPDS card No. P04-0850). In comparison, a mixture (labeled as S_{SM7}) of Ni nanopowders and β -Ni(OH)₂ (JCPDS card No. 14-0117) were obtained with a 2T magnetic field. The formation of metallic Ni, which differed from cobalt hydroxide formation in the absence of magnetic field under the same reaction condition, was likely caused by Ni reduction by hydrazine that can serve as a mild reducing reagent. These experiments are not able to confirm generic magnetic field effects of the Ni(OH)₂ phases control. However, the variation of the products after introduction of a magnetic field (Ni plus β -Ni(OH)₂ @ 2T magnetic field versus Ni @ no magnetic field) still suggests its effects.



Figure S9. XRD patterns of sample S_{S7} using NiCl₂ precursor prepared in the absence of magnetic field. (a), and S_{SM7} prepared in the presence of 2T magnetic field. (b).

Element	Sample S ₀	Sample S _{0.2T}	Sample S _{2T}
	(Atomic %)	(Atomic %)	(Atomic %)
C K	14.83	14.29	11.11
ОК	33.49	33.33	28.89
Co L	30.62	26.29	22.22
Cl K	21.05	26.09	37.78

Table S1. Atomic percentage of Co, Cl, O and C in sample S_0 , $S_{0.2T}$ and S_{2T} .

Materials		specific capacitance values at different current density	cycling stability
Our work	S _{2T}	885 F/g at 1 A/g,	91% of initial capacitance
		699 F/g at 10 A/g	remains after 1500 cycles
Our work	S _{0.2T}	593 F/g at 1 A/g,	83% of initial capacitance
		421 F/g at 10 A/g	remains after 1500 cycles
Our work	S ₀	388 F/g at 1 A/g,	70% of initial capacitance
		260 F/g at 10 A/g	remains after 1500 cycles
Ref. 1	g-Co(OH)	396 F/g at 1 A/g	a specific capacitance
	nenoshoots	232 F/g at 10 A/g	degradation is ca. 2% after
	nanosneets		1000 continuous cycling
Ref. 2	flower-like α-	440 F/g at 1 A/g,	no loss in capacitance over
	Co(OH) ₂	231 F/g at 10 A/g	5000 cycles
Ref. 3	g-Co(OH).	642 5 F/g at 1 A/g	no obvious capacitance
	nanowire arrays	351 F/g at 10 A/g	decrease appearing over
			3000 cycles
Ref. 4	β-Co(OH) ₂	351 F/g at 1 A/g,	86.3% of initial capacitance
	nanowires	325 F/g at 10 A/g	remains after 5000 cycles
Ref. 5	porous β-	$A16 \mathbf{E}/\mathbf{g}$ of $1 \mathbf{A}/\mathbf{g}$	retention of specific
	Co(OH) ₂	410 F/g at 1 A/g,	capacitance is about 93%
	nanostructure	520 F/g at 5 A/g	after 500 cycles
Ref. 6	β-Co(OH) ₂	562 F/g at 2 A/g,	after 3000 cycles, 88% of
	nanocone arrays	390 F/g at 8 A/g	initial capacitance remains

Table S2. Electrochemical performances of S_{2T} (magnetic field-assisted synthesized Co(OH)₂) in this work and several representative results from recent published works.

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