Electronic Supporting Information

Understanding the crystal structure-dependent electrochemical capacitance of spinel and rock-salt Ni-Co oxides via density function theory calculations

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1. Experimental methods

1.1 Sample preparation

The sample of $NiCoO_2$ was synthesized according to our previous work.[1] Typically, 1.5 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 1.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ and 15 mmol of urea were dispersed in 40 mL of ethanol and stirred with magnetic stirrer to obtain a clear solution. Then, the resulting solution was poured into Teflon-lined stainless steel autoclave (50 mL in volume), then reserved at 100 ºC for 8 h. After completion of the reaction, the obtained $NiCoO_2$-precursor was collected by centrifuge and washed thoroughly then dried at 60 ºC for 12 h. Finally, the rock-salt $NiCoO_2$ was obtained by calcinating the $NiCoO_2$-precursor at 300 ºC in N_2 atmosphere for 3 h with a heating rate of 1 ºC min^{-1}. The precursor of $NiCo_2O_4$ sample was prepared at 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$ following the above method. Then the $NiCo_2O_4$-precursor was annealed in air atmosphere to obtain spinel $NiCo_2O_4$, while other parameters were kept unchanged.

1.2 Materials Characterizations

X-ray diffraction (XRD) patterns were recorded on a multipurpose XRD system with a Cu K*a* radiation (Rigaku Ultima IV, Japan) to examine crystalline phases. The morphologies and structures of the as-prepared electrode materials were characterized by field-emission scanning electron microscopy (FESEM, JEOL 6300F) and transmission electron microscopy (TEM, JEOL JEM 2100 system).

1.3 Electrochemical measurements

The electrochemical performance of cyclic voltammetry (CV) and chronopotentiometry (CP) tests for the samples were all carried out on a electrochemical workstation (IVIUM, Netherlands), using a three-electrode system with a working electrode, a Pt foil counter electrode and a saturated calomel electrode (SCE) reference electrode in 2 M potassium hydroxide (KOH) aqueous solution at room temperature. The working electrodes were prepared by coating a piece of nickel foam (1 cm^2) with the slurry containing the electroactive materials, acetylene black and polytetrafluoroethylene in a weight ratio of 5 : 2 : 1. For the electrochemical measurements, the mass loading of electroactive material in each electrode was 5.0 mg. The specific capacitance (SC) for the three-electrode configuration were calculated from the CP curves using SC = It/mV, where m (g) is the mass of electrode material, I (A g^{-1}), t (s) and V (V) are current density, discharge time, and voltage range.

Reference

1 Z. Wang, Z. Zhao, Y. Zhang, G. Pang, X. Sun, J. Zhang, L. Hou and C. Yuan, *J. Alloys and Compd.*, 2019, **779**, 81-90.

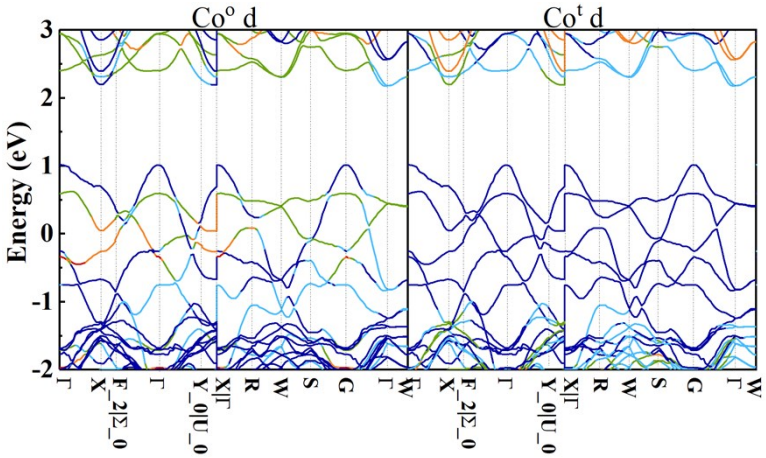

Fig. S1 The contribution of *d*-orbital of all Co^o and Co^t atoms to the band structure near the Fermi-level in $NiCo_2O_4$. The energy zero is set at the Fermi-level.

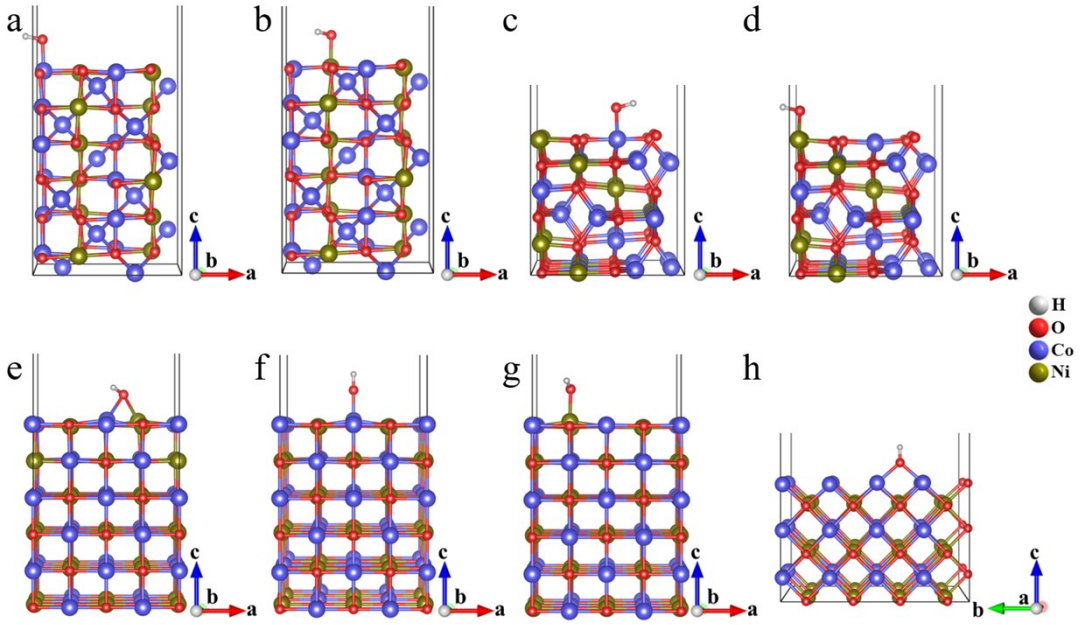

Fig. S2 Configurations of the preferred hydroxyl adsorption on the top of (a) Co, (b) Ni in $NiCo_2O_4(100)$; (c) Co, (d) Ni in $NiCo_2O_4(110)$; (e) bridge between Ni and Co, top of (f) Co, (g) Ni in $NiCoO_2(100)$ and (h) bridge between two Co atoms in $NiCoO_2(110)$.

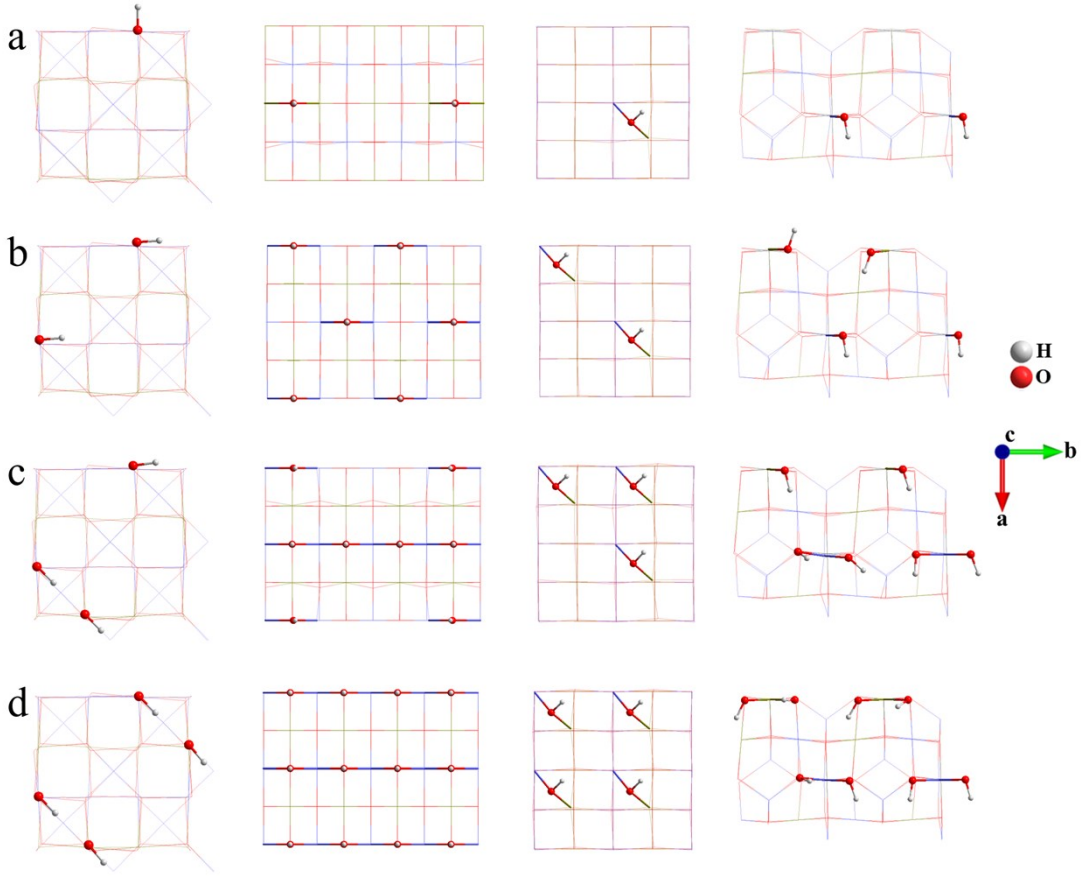

Fig. S3 Configurations of the hydroxyl adsorption on the studied surfaces at (a) 25 %; (b) 50 %; (c) 75 % and (d) 100 % coverage.

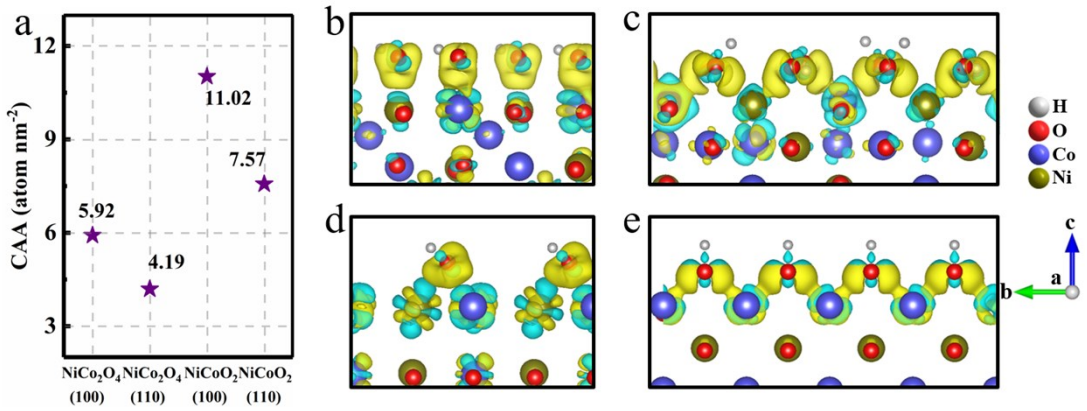

Fig. S4 (a) The CAA of electroactive Ni/Co atoms for all the calculated surfaces. Charge density difference of (b) $NiCo_2O_4(100)$, (c) $NiCo_2O_4(110)$, (d) $NiCoO_2(100)$ and (e) $NiCoO_2(110)$ before and after hydroxyl adsorption (Isosurface=0.01 e/Å^3). Yellow and blue represent electron accumulation and depletion, respectively.

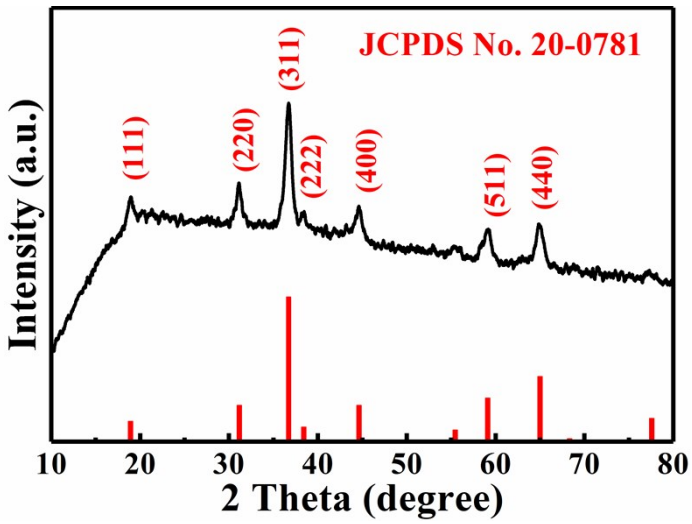

Fig. S5 XRD patterns of the $NiCo_2O_4$.

As shown in Fig. S5, the XRD analysis indicated that all peaks can be well indexed to the cubic $NiCo_2O_4$ (JCPDS No. 20-0781) with spinel structure.

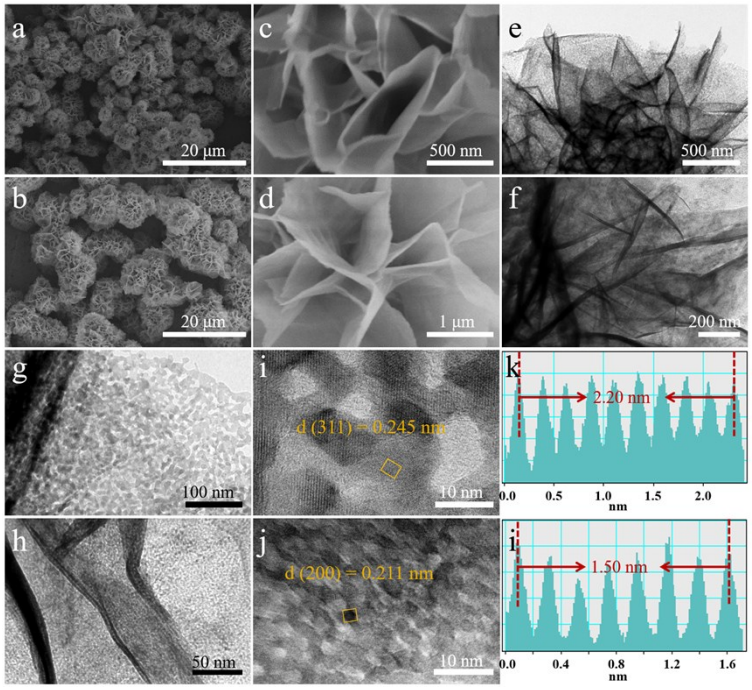

Fig. S6 (a, b) Low and (c, d) high magnified FESEM images, (e, f) TEM and (g, h) high-magnification TEM, (i, g) HRTEM, (k, l) interplanar spacing of $NiCo_2O_4$ and $NiCoO_2$ respectively. The image in panels (k, l) are taken from the orange rectangle region in panels (I, j).

As shown in FESEM images with low-magnification (Fig. S6a-d), both the spinel $NiCo_2O_4$ and rock-salt $NiCoO_2$ samples exhibit the similar microflower morphology, which with homogeneous shape and average diameter of 3-4 μm. The TEM images further demonstrate the similar morphology between $NiCo_2O_4$ and $NiCoO_2$, which is formed by numerous continuous nanoparticles (Fig. S6e-j). HRTEM images (Fig. S6i, j) and corresponding analysis (Fig. S6i-l) demonstrate that the lattice fringes with an interplanar spacing of about 0.245 and 0.211 nm matched well with the (311) and (200) plane of $NiCo_2O_4$ and $NiCoO_2$, respectively.

Table S1 The calculated lattice constants of bulk phases and selected surfaces for the p(1×1) cell. The values taken from JCPDS no. 20-0781 for $NiCo_2O_4$ and 10-0188 for $NiCoO_2$ are included in parenthesis for comparison.

Bulk/ Surface	$NiCo_2O_4$	$NiCoO_2$	$NiCo_2O_4$ (100)	$NiCo_2O_4$ (110)	$NiCoO_2$ (100)	$NiCoO_2$ (110)
a (Å)	8.22 (8.11)	4.26 (4.24)	8.22	8.22	4.26	4.26
b (Å)	8.22 (8.11)	4.26 (4.24)	8.22	11.62	4.26	6.02
c (Å)	8.22 (8.11)	4.26 (4.24)	/	/	/	/