

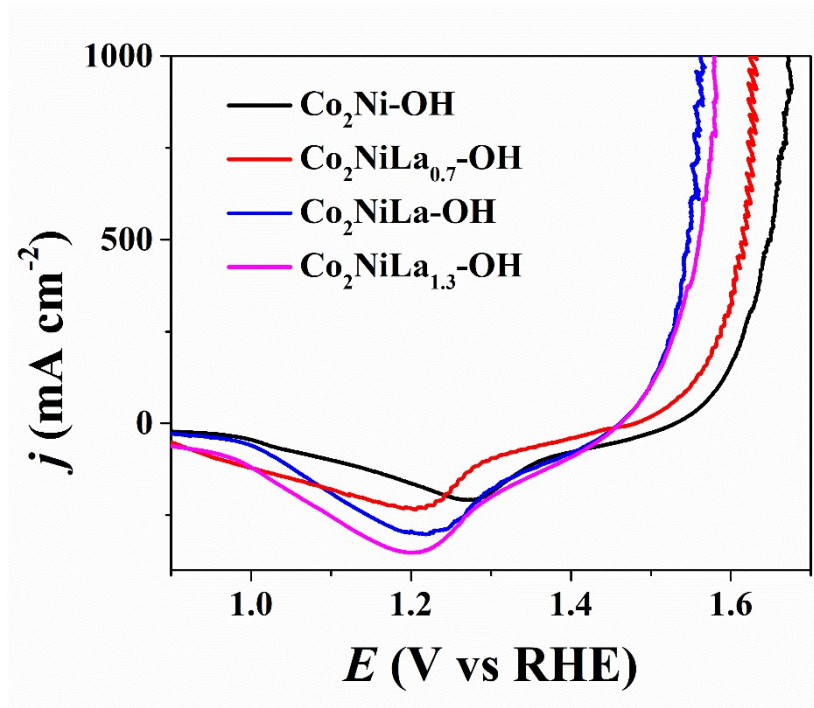
## Supporting Information

**A robust strategy to boost the proton transfer of heterogeneous catalysts for efficient and sustainable water oxidation towards practical applications**

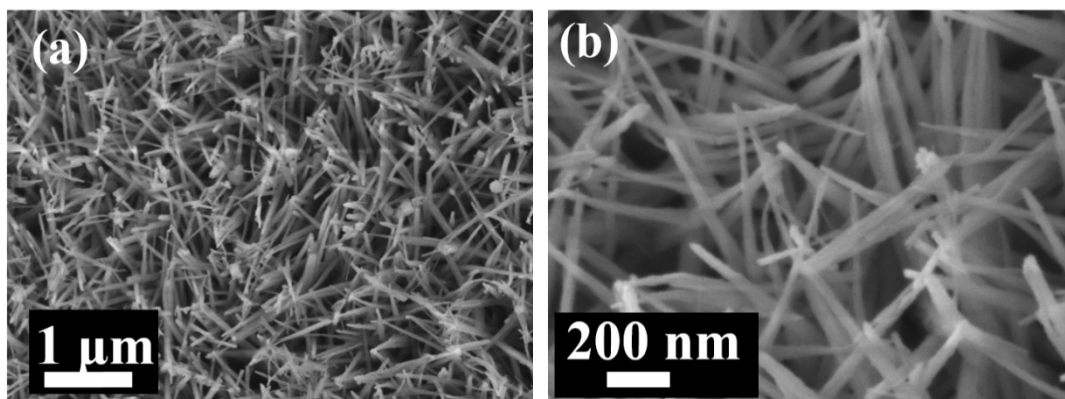
Qihua Huo, Jianyong Cao, Lingren Mi, Jiaxing Shao, Miaoyuan Lv, Xingbao Chen, Hengpan Yang, Xiaoyan Chai, Qi Hu\* and Chuanxin He\*

Department of Chemistry, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong 518060, China.

E-mail: hq2016@szu.edu.cn; hecx@szu.edu.cn



**Figure S1.** LSV of  $\text{Co}_2\text{Ni-OH}$  with different content of  $\text{La}^{3+}$ , such as  $\text{Co}_2\text{Ni-OH}$  without  $\text{La}^{3+}$ ,  $\text{Co}_2\text{NiLa}_{0.7}\text{-OH}$ ,  $\text{Co}_2\text{NiLa-OH}$ , and  $\text{Co}_2\text{NiLa}_{1.3}\text{-OH}$  (0.7, 1, and 1.3 represent the content of  $\text{La}^{3+}$ ), for OER in 1 M KOH.



**Figure S2.** SEM images of  $\text{Co}_2\text{Ni-OH}$ .

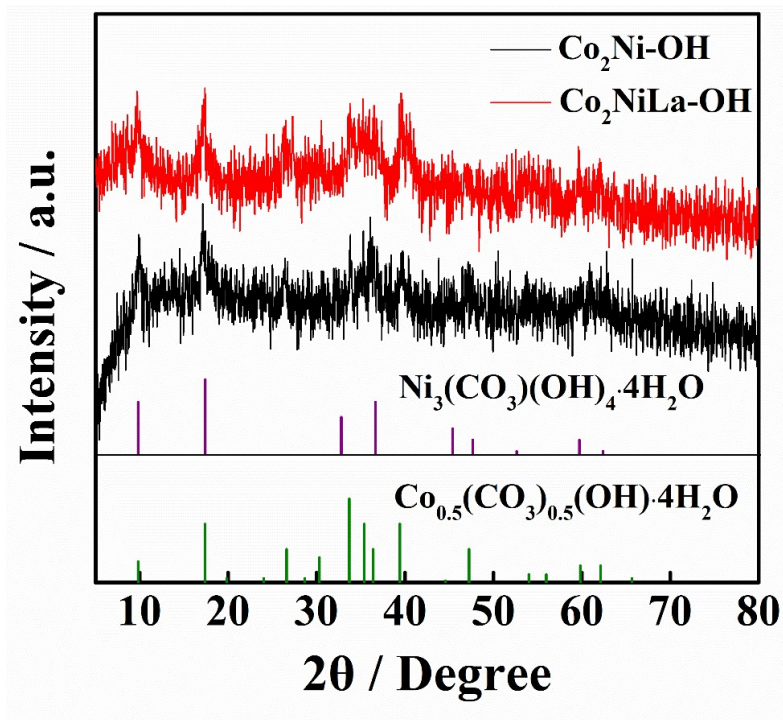


Figure S3. XRD patterns of  $\text{Co}_2\text{Ni-OH}$ , and  $\text{Co}_2\text{NiLa-OH}$ .

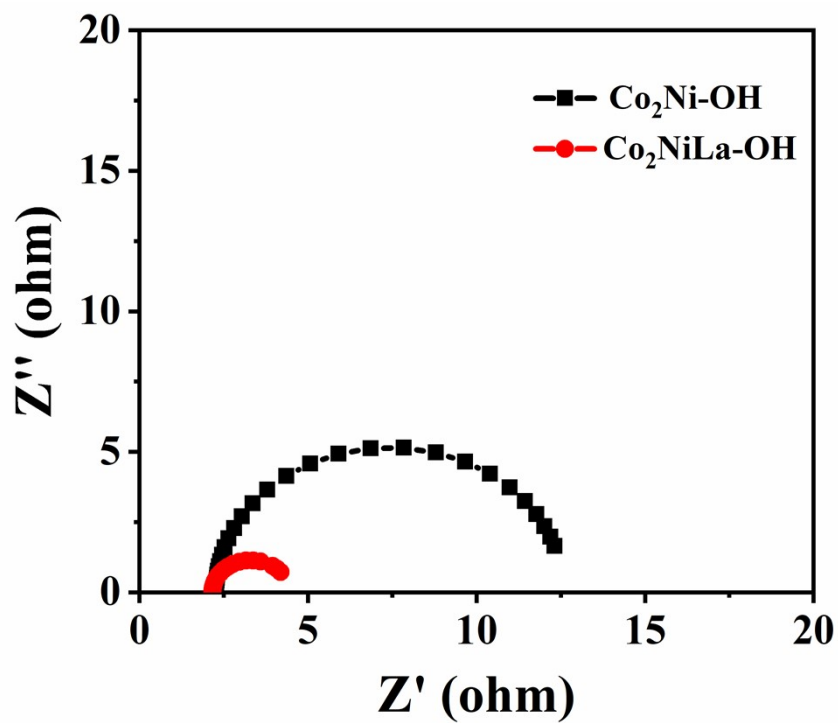
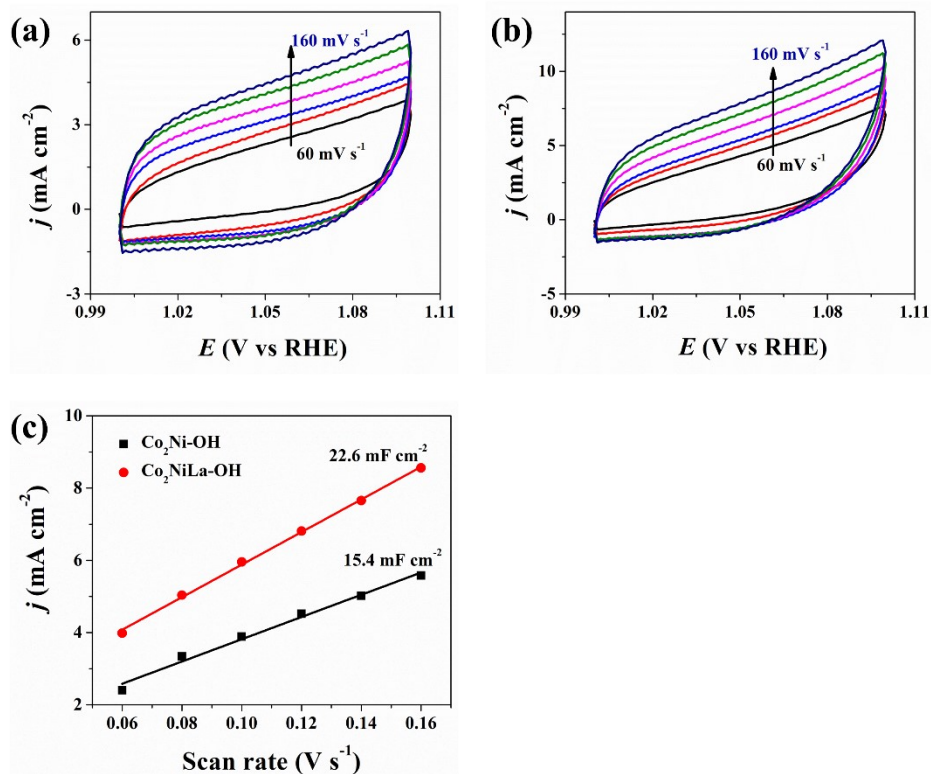
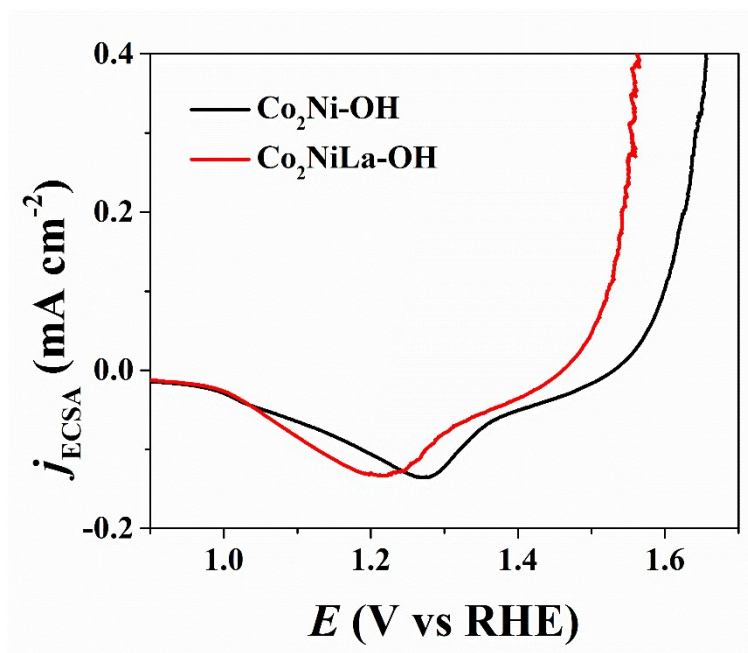


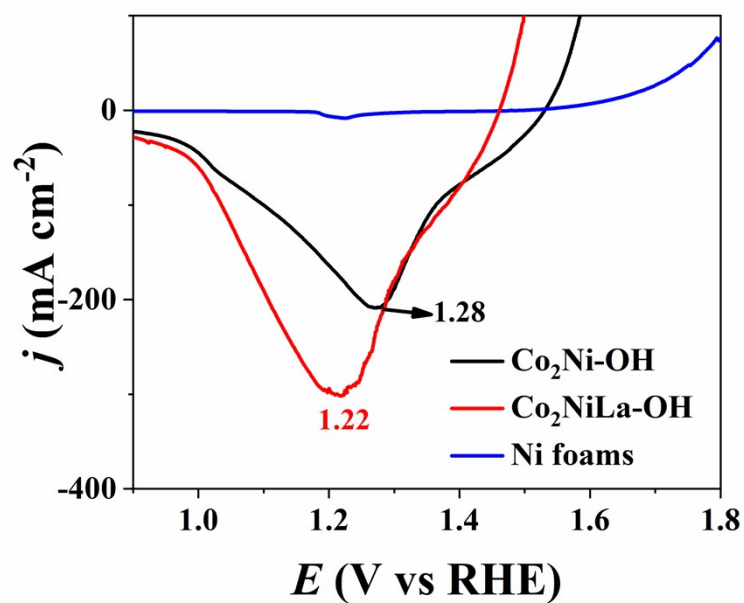
Figure S4 Electrochemical impedance spectroscopy (EIS) measurements on the  $\text{Co}_2\text{NiOH}$  and  $\text{Co}_2\text{NiLa-OH}$



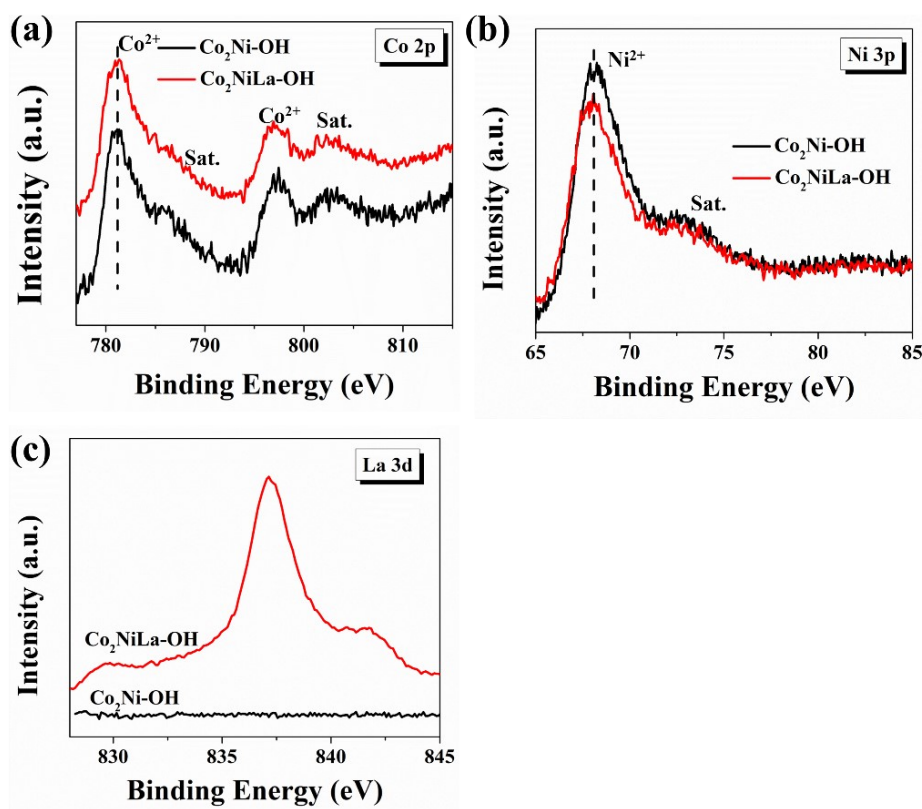
**Figure S5** CV of (a) Co<sub>2</sub>Ni-OH, and (b) Co<sub>2</sub>NiLa-OH at different scan rates. (c) Curves of capacitance  $\Delta j$  ( $|j_{\text{charge}} - j_{\text{discharge}}|$ ) as a function of different scan rates.



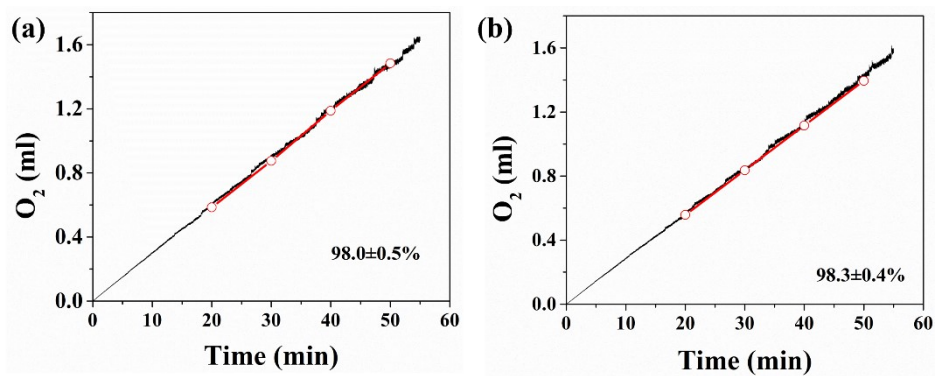
**Figure S6** LSV of Co<sub>2</sub>Ni-OH and Co<sub>2</sub>NiLa-OH after normalizing ECSA in 1 M KOH.



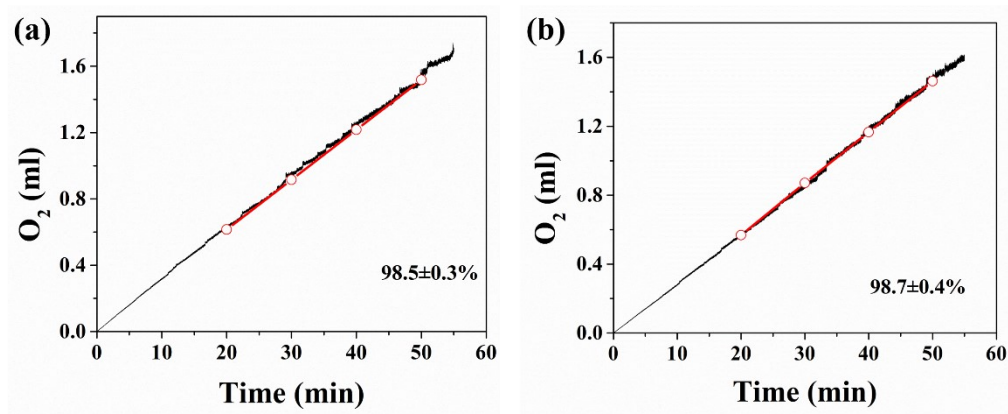
**Figure S7** Enlarged view of oxidation peak for the  $\text{Co}_2\text{Ni-OH}$ ,  $\text{Co}_2\text{NiLa-OH}$ , and Ni foams during the process of OER.



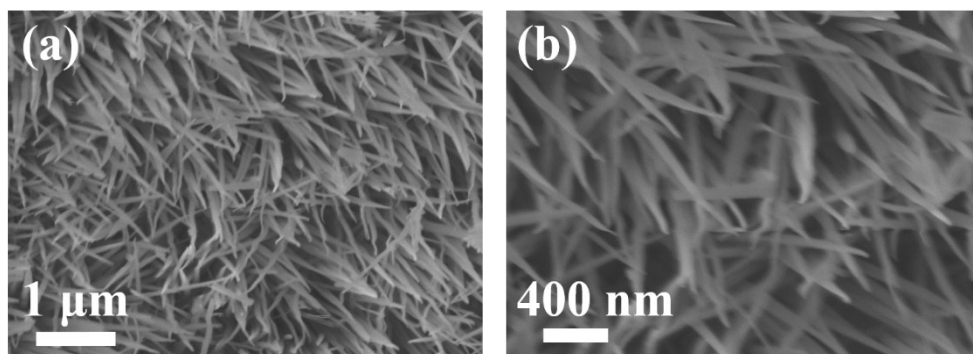
**Figure S8** XPS spectra of (a) Co 2p, (b) Ni 3p, and (c) La 3d for the  $\text{Co}_2\text{Ni-OH}$ , and  $\text{Co}_2\text{NiLa-OH}$ .



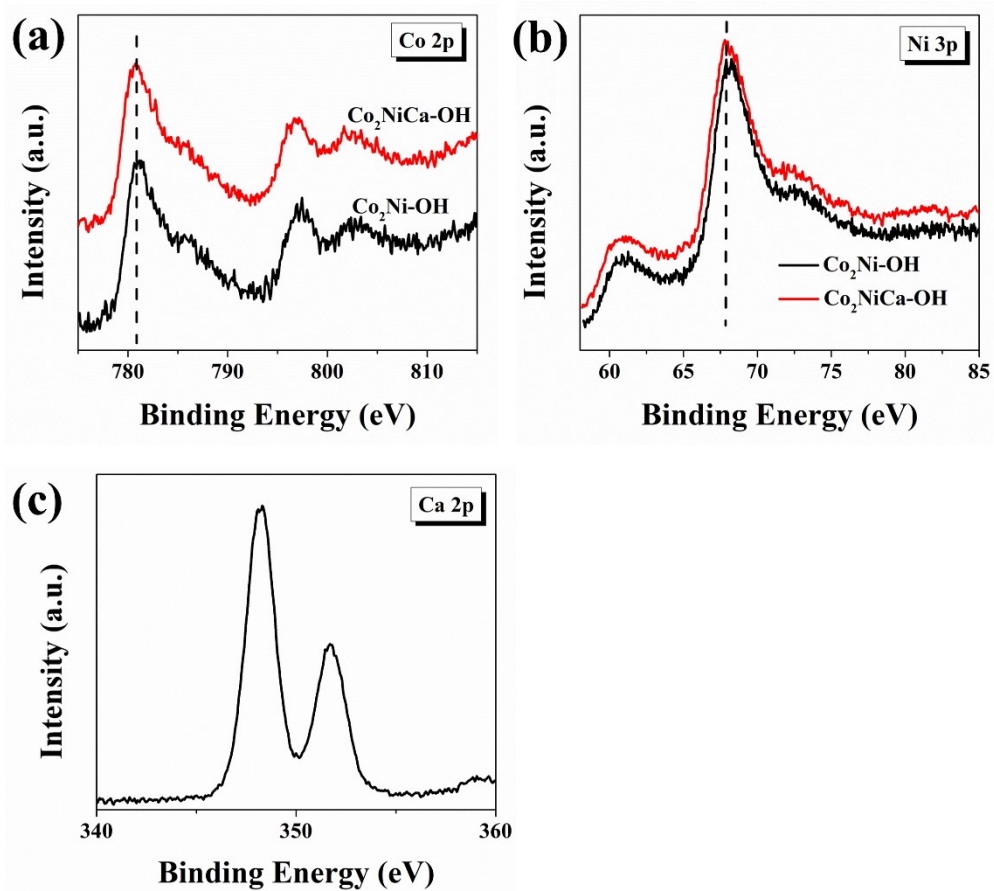
**Figure S9** Faradaic efficiencies of (a)  $Co_2Ni-OH$  and (b)  $Co_2NiLa-OH$  in 1 M NaOH at the current of  $\sim 6.0$  mA.



**Figure S10** Faradaic efficiencies of (a)  $Co_2Ni-OH$  and (b)  $Co_2NiLa-OH$  in 1 M NaOD  $D_2O$  at the current of  $\sim 6.0$  mA.

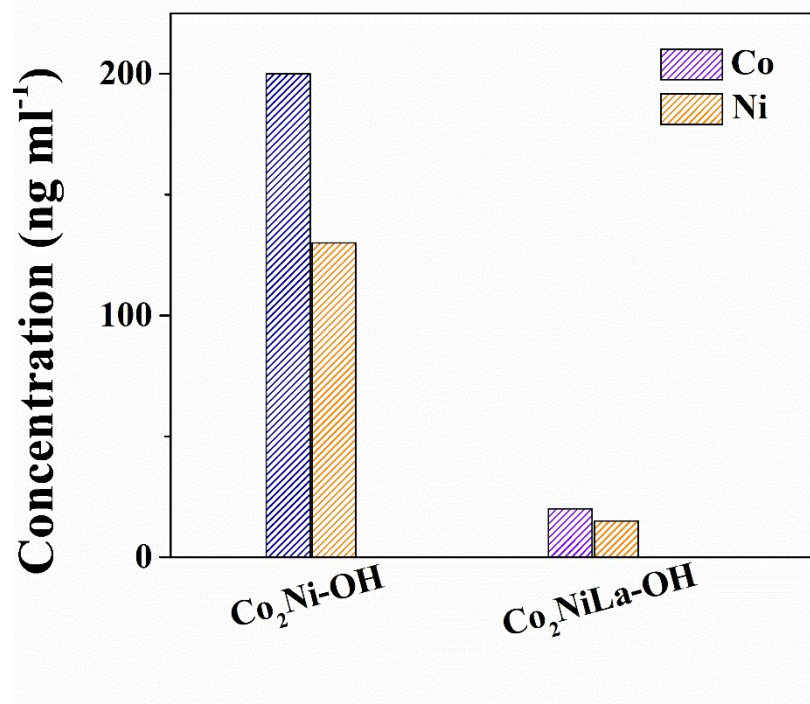


**Figure S11** SEM images of  $Co_2NiCa-OH$ .

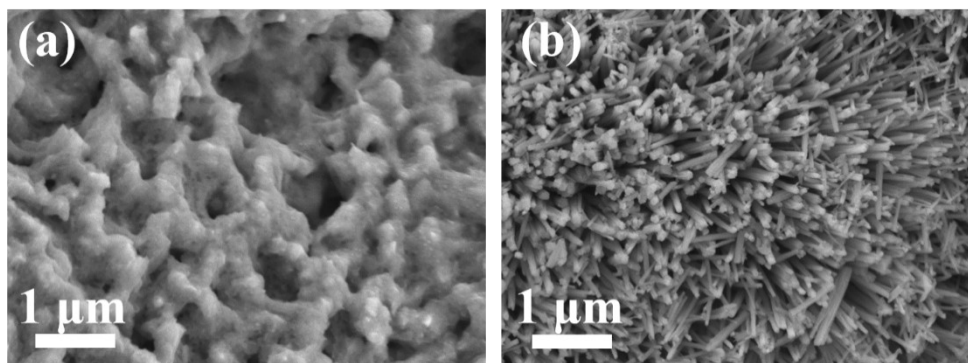


**Figure S12** XPS spectra of (a) Co 2p, (b) Ni 3p, and (c) Ca 2p for the sample of  $\text{Co}_2\text{NiCa-OH}$ .

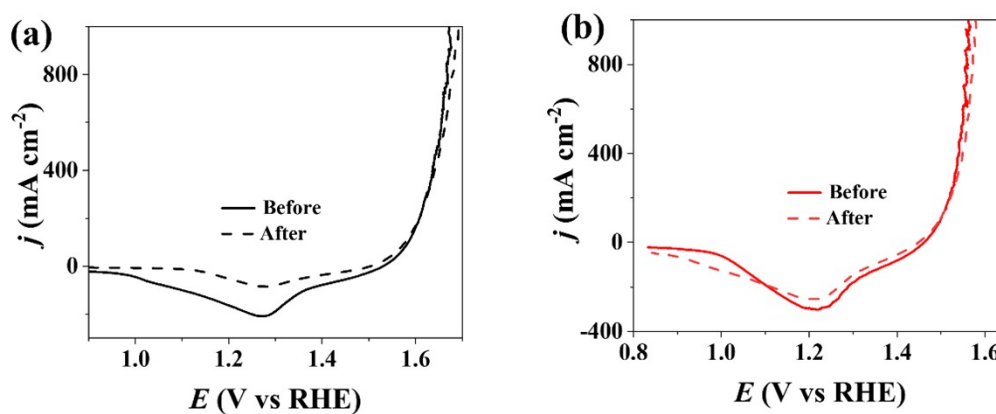




**Figure S13** Content of Co<sup>2+</sup> and Ni<sup>2+</sup> in the electrolyte after stability tests of Co<sub>2</sub>Ni-OH, and Co<sub>2</sub>NiLa-OH.



**Figure S14** SEM images of (a) Co<sub>2</sub>Ni-OH, (b) Co<sub>2</sub>NiLa-OH after stability tests under harsh conditions (at 60 °C, in 6 M KOH).



**Figure S15** LSV curves of (a) Co<sub>2</sub>Ni-OH and (b) Co<sub>2</sub>NiLa-OH before and after 1000 times of potential cycles.

### Note 1 Determining the reaction order of phosphate radical

As previously reported, for the OER follows the base-dependent pathways, the rate of OER can be determined by the follow equation<sup>[S1-S2]</sup>:

$$k_{cat} = k_{H_2O} + k_B[B] \quad (1)$$

where  $k_{cat}$  is the total reaction rate of OER on an eletrocatalyst,  $k_{H_2O}$  and  $k_B$  represent the OER reaction rate under conditions of pure water without additional base in the electrolyte and water with additional base (i.e., phosphate) as proton acceptors in the electrolyte, respectively, and  $[B]$  is the concentration of additional base.

Considering that  $k_{cat}$  is positively proportional to the obtained OER current density, the  $k_{cat}$  can be expressed as turnover frequency (TOF). Thus, the equation (1) can be further change to

$$k_{cat} = \text{TOF}_\eta = \left[ \frac{jA}{4FmA} \right]_\eta = k_{H_2O} + k_B[B] \quad (2)$$

where  $j$  is the current density at a specified overpotential ( $\eta$ ),  $A$  is the surface area of electrode,  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $m$  is the number of active sites (mol cm<sup>-2</sup>).

In the equation 2, the  $k_{H_2O}$  is not changed with the  $[B]$ , and thus it can be considered as a constant. Accordingly, the  $j$  should be first order dependent with the concentration of addition base. Therefore, in our cases, the current densities of Co<sub>2</sub>Ni-OH and Co<sub>2</sub>NiLa-OH should be first order dependent on the concentration of PO<sub>4</sub><sup>3-</sup>.

### References

- [S1] Chen, Z. *et al.* Concerted O atom–proton transfer in the O—O bond forming step in water oxidation. *Proc. Natl Acad. Sci. USA* **107**, 7225-7229, doi:10.1073/pnas.1001132107 %J Proceedings of the National Academy of Sciences (2010).

- [S2] Li, W. *et al.* A bio-inspired coordination polymer as outstanding water oxidation catalyst via second coordination sphere engineering. *Nat. Commun.* **10**, 5074, doi:10.1038/s41467-019-13052-1 (2019).

