v# Electronic Supplementary Material (ESI) for *Journal of Materials Chemistry A*
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Ultrahigh-Rate-Capability of A Layered Double Hydroxide Supercapacitor Based on Self-Generated Electrolyte Reservoir

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Supplementary Figures

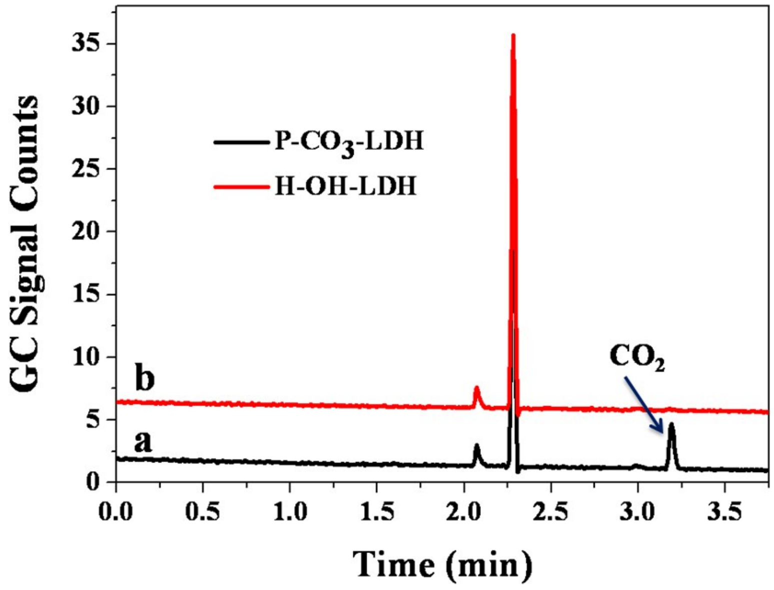

Fig. S1. Gas chromatogram (GC) spectrum of the P-CO_3-LDH and H-OH-LDH.

Headspace gas chromatography (HSGC) analysis was carried out to further confirm the anion exchange from CO_3^{2-} to OH^- after a calcination-rehydration process (Figure S1). For the P-CO_3-LDH precursor, an obvious peak of CO_2 at 3.2 min (retention time) is observed from the gas chromatography spectrum, along with two other signals (2.1 and 2.3 min) of carrier gas. After rehydration, the CO_2 signal disappears completely, demonstrating the absence of CO_3^{2-} in the rehydrated sample.

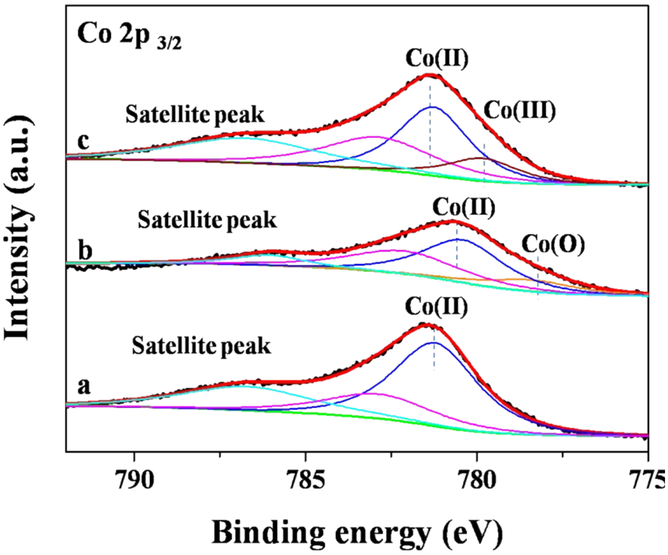

Fig. S2. Co $2p_{3/2}$ XPS spectra of (a) P-CO_3-LDH, (b) Co-Al_2O_3-CoO and (c) H-OH-LDH sample.

X-ray photoelectron spectroscopy (XPS) was used to monitor the chemical state of the elements during a calcination-rehydration process. Figure S2 displays the XPS results of Co $2p_{3/2}$ of P-CO_3-LDH, Co-Al_2O_3-CoO and H-OH-LDH sample. For P-CO_3-LDH nanoplates array, the binding energy is located at 781.2 eV (line a), attributed to Co (II) in LDH host layer. After calcination in H_2 atmosphere, the Co $2p_{3/2}$ peak shifts to lower energy region (780.5 eV) (line b), corresponding to the Co (II) state in CoO form; and a new peak emerges at 778.2 eV ascribed to Co metal. For the sample of H-OH-LDH, the Co (II) peak shifts to almost the same energy level with that of P-CO_3-LDH (line c). Meanwhile, a decomposed peak at 779.8 eV attributed to the Co (III) in hydroxide is observed, indicating that trace part of Co (II) is oxidized to Co (III) after rehydration in aqueous alkali.

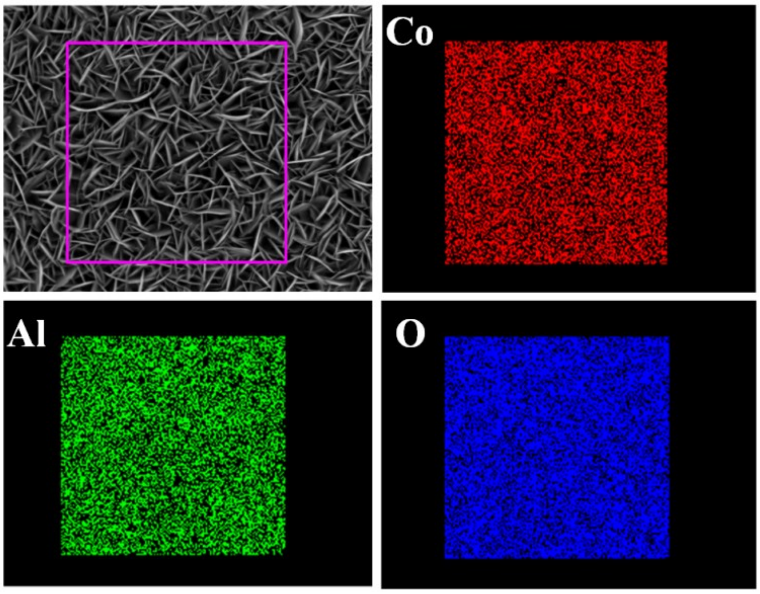

Fig. S3. SEM image and EDX mapping of the P-CO_3-LDH array.

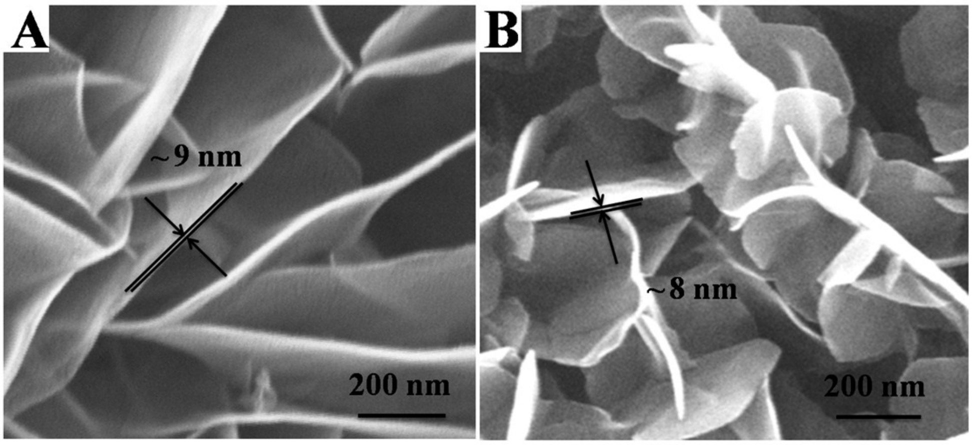

Fig. S4. SEM images of (A) P-CO_3-LDH and (B) H-OH-LDH electrode.

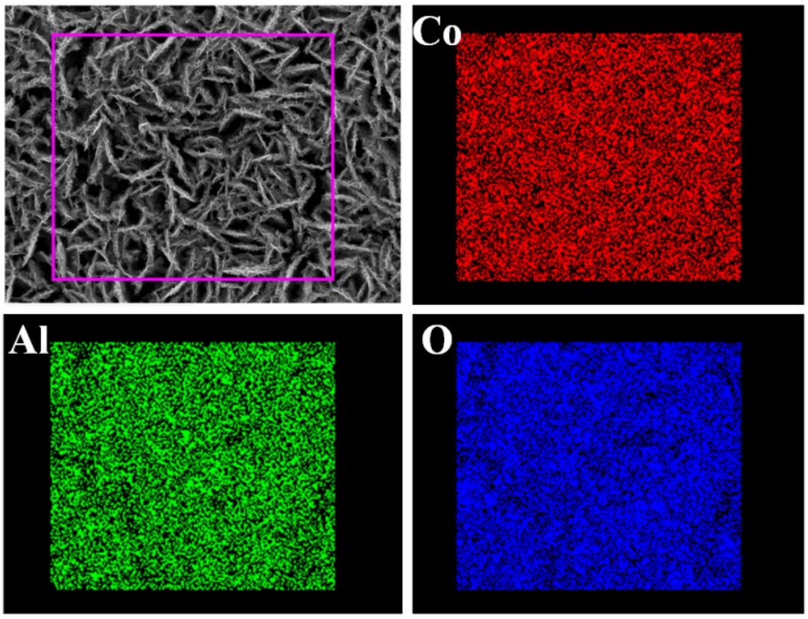

Fig. S5. SEM image and EDX mapping of the H-OH-LDH array.

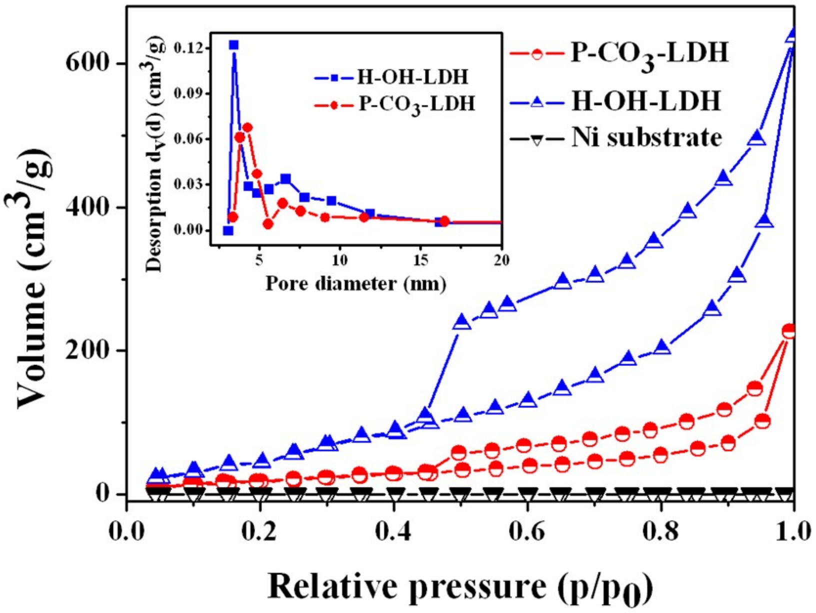

Fig. S6. N_2 adsorption-desorption isotherms of Ni substrate, P-CO_3-LDH and H-OH-LDH sample. The inset picture shows pore size distribution of P-CO_3-LDH and H-OH-LDH sample.

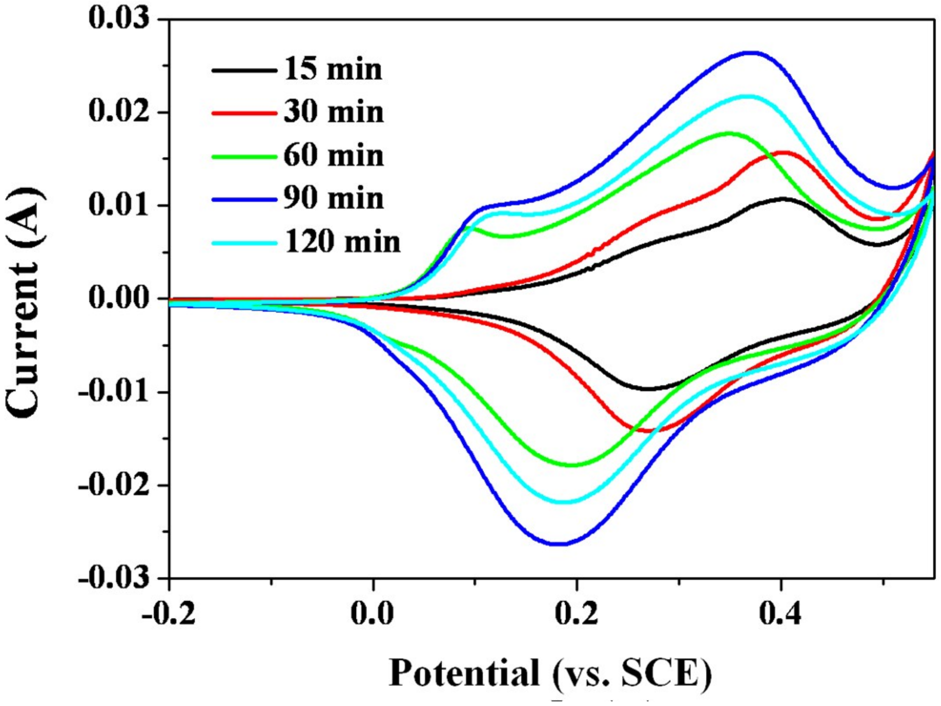

Fig. S7. Cyclic voltammetry (CV) curves of H-OH-LDH electrodes with different hydration time in a three-electrode system (reference electrode: standard calomel electrode, electrolyte: 1.0 M KOH, scan rate: 50 mV/s).

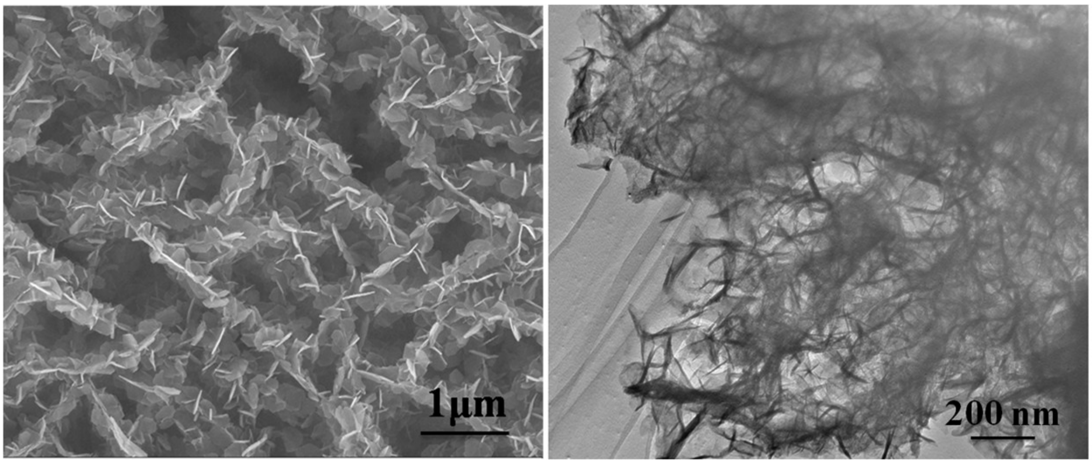

Fig. S8. SEM and TEM images of the H-CO_3-LDH array.

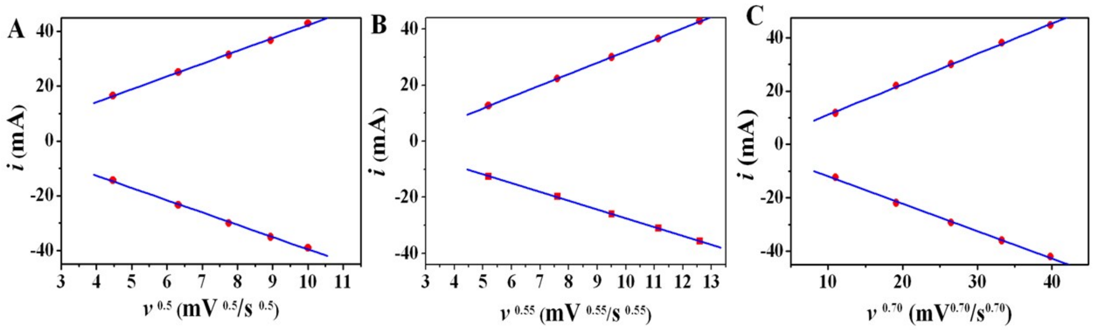

Fig. S9. The cathodic/anodic peak current as a function of the scan rates for (A) P-CO_3-LDH, (B) H-CO_3-LDH and (C) H-OH-LDH electrode.

The ion diffusion kinetics in P-CO_3-LDH, H-CO_3-LDH and H-OH-LDH electrode was quantified based on CV curves by the following equation:

$$i = av^b$$

where *i* is the current (mA); *v* is the scan rate (mV/s); and *a*, *b* are adjustable values. A *b*-value of 0.5 indicates that the redox reaction is controlled by semi-infinite linear diffusion; whereas *b*-value of 1 indicates the reaction is surface-controlled.[S1, S2] To obtain decent values for *b*, the peak current value versus the exponential of the scan rate was plotted with b = 0.50, 0.55 and 0.70 for P-CO_3-LDH, H-CO_3-LDH and H-OH-LDH electrodes, respectively (Figure S9). The largest *b* value of H-OH-LDH electrode is ascribed to the accelerated ion diffusion to the inner surface of LDH lamella, in accordance with the EIS analysis of these electrodes (Figure 5F).

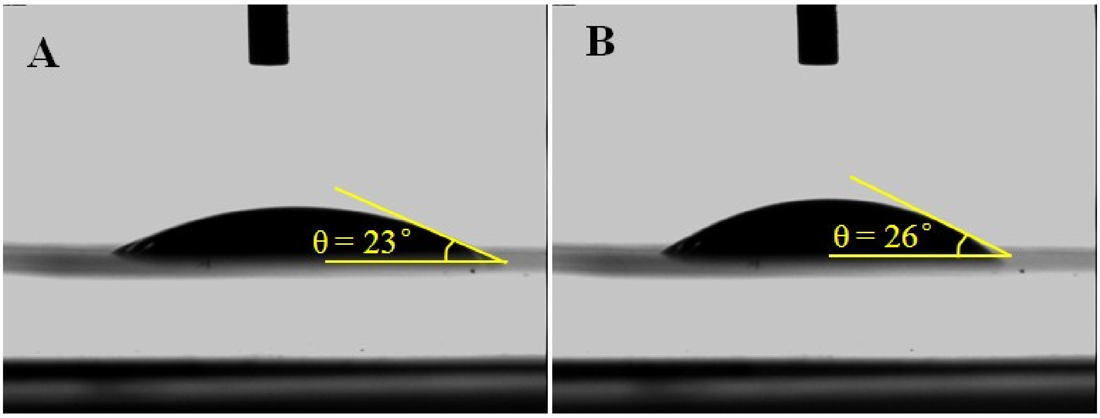

Fig. S10. Contact angle measurement on the surface of (A) P-CO_3-LDH film and (B) H-OH-LDH film.

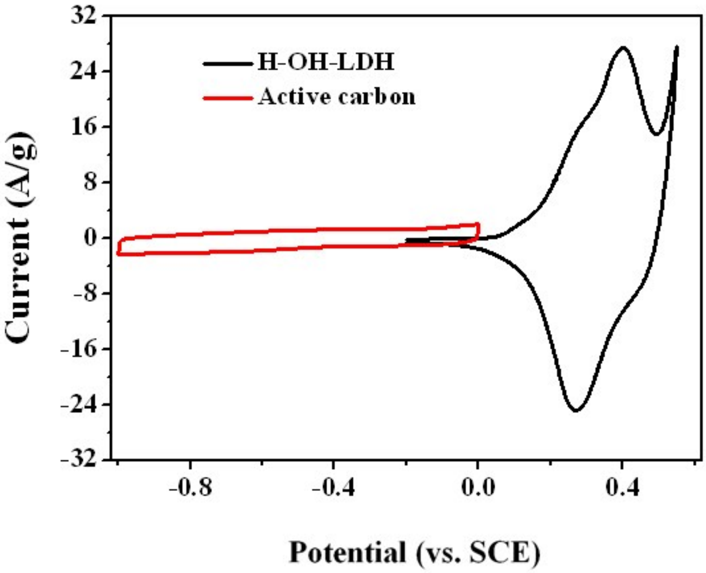

Fig. S11. CV curves of the active carbon and H-OH-LDH electrode in a three-electrode system.

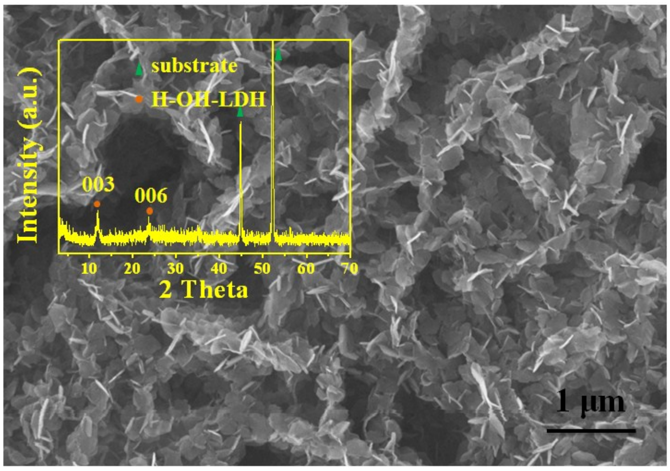

Fig. S12. XRD and SEM image of the H-OH-LDH after 2000 change-discharge cycles.

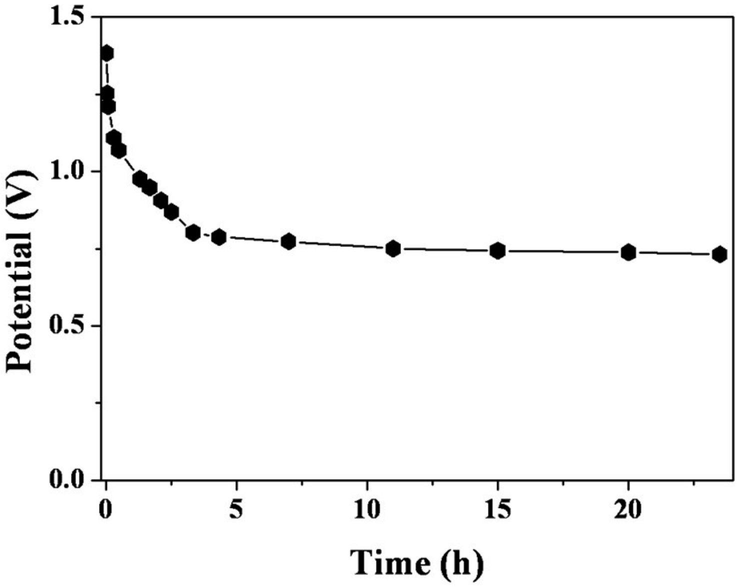

Fig. S13. Self-discharge curve of the H-OH-LDH//AC SC device after charged to 1.5 V for 24 h.

References

[S1] H. Lindström, S. Södergren, A. Solbrand, H. Rensmo, J. Hjelm, A. Hagfeldt, S. Lindquist. *J. Phys. Chem. B*, 1997, **101**, 7717.

[S2] V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abruna, P. Simon, B. Dunn, *Nat. Mater.*, 2013, **12**, 518.