Supporting Information for

# 3D Hierarchical Co-Al Layered Double Hydroxides with Long-term Stabilities and High Rate Performances in Supercapacitors

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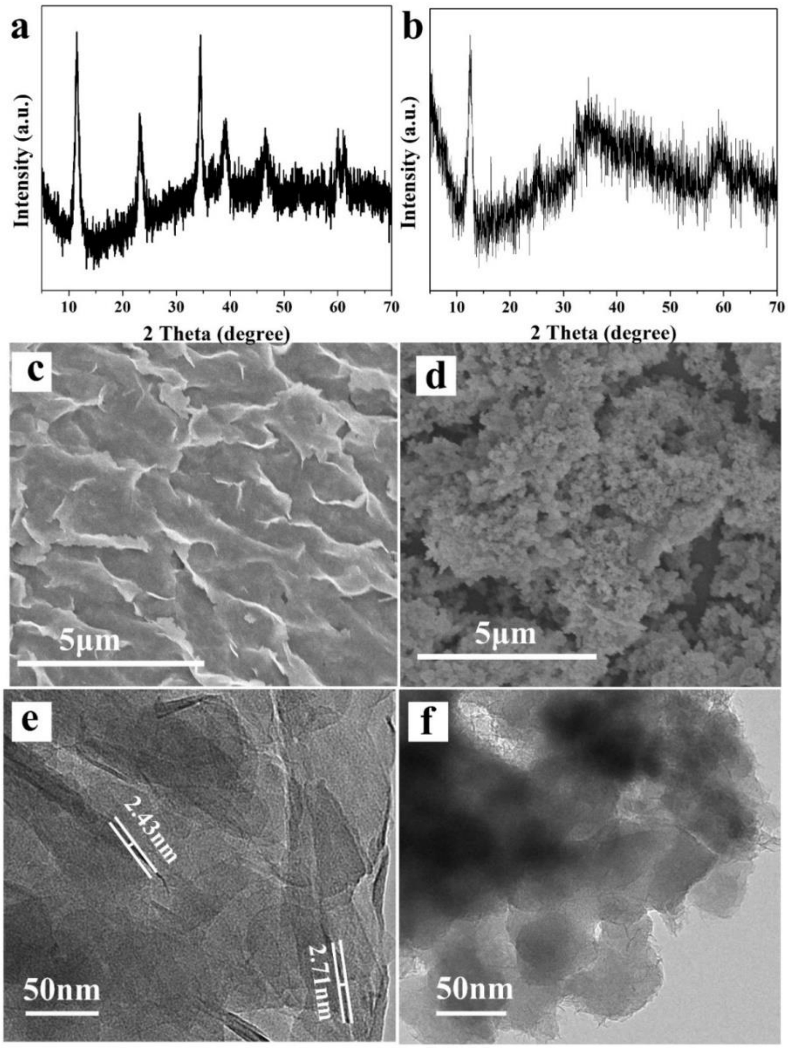


**Fig. S1** XRD, SEM and TEM images of 2D Co-Al-LDHs (**a, c, e**) and 0D Co-Al-LDHs (**b, d, f**)

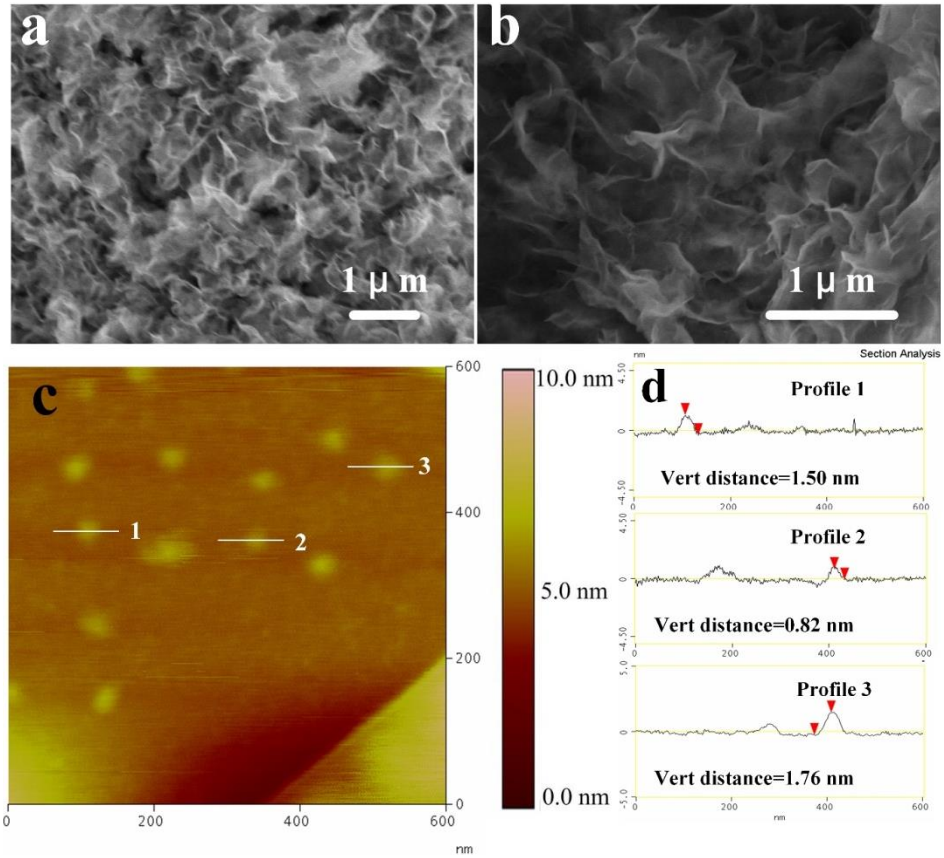


**Fig. S2** SEM (**a-b**), AFM (**c**) and height profiles (**d**) images of atomically thin layered 3D Co-Al-LDHs. Profiles 1, 2 and 3 correspond to the numbered lines in a, respectively

To further determine the thickness of the as-prepared 3D Co-Al-LDHs nanosheets, samples dispersed on a mica wafer have been observed by Atomic Force Microscopy (AFM). The cross-sectional analysis corresponding to the highlighted profiles 1, 2 and 3 in the topography image clearly shows the average height of LDHs with less than 2 nm and smooth rounded shapes of ca. 54, 35, and 70 nm.

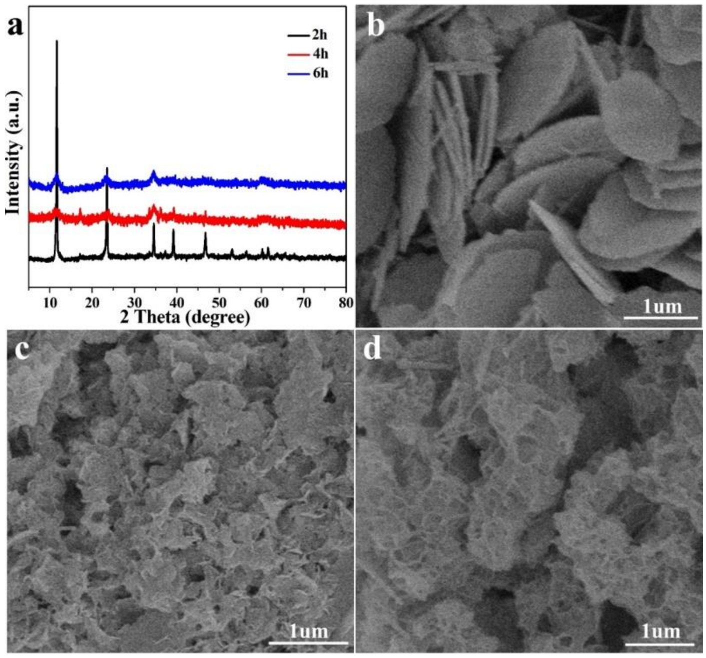


**Fig. S3** (**a**) XRD of the target product Co-Al-LDHs (in 40 mL deionized water and 40 mL butyl alcohol) with different reaction time, and the corresponding SEM of 2 h (**b**), 4 h (**c**), 6 h (**d**)

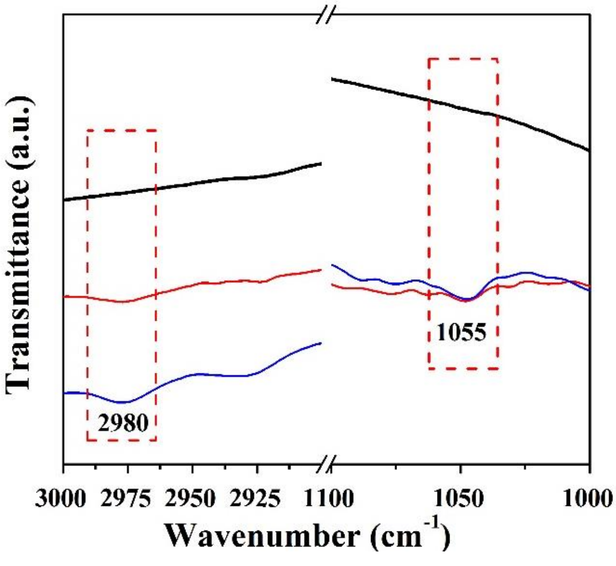


**Fig. S4** Detailed FTIR spectra in the range of 3000-2900 $cm^{-1}$ and 1100-1000 $cm^{-1}$

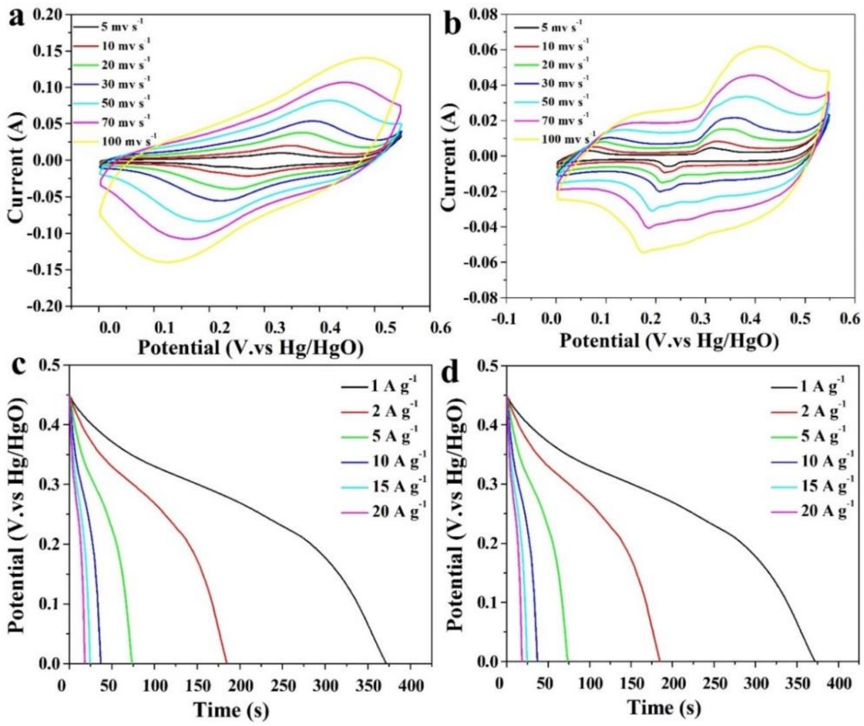


**Fig. S5** CV curves of 2D Co-Al-LDHs (**a**), 0D Co-Al-LDHs (**b**) at different scan rates in 2 M KOH aqueous electrolyte, and galvanostatic charge–discharge curves at different current densities of 2D Co-Al-LDHs (**c**) and 0D Co-Al-LDHs (**d**)

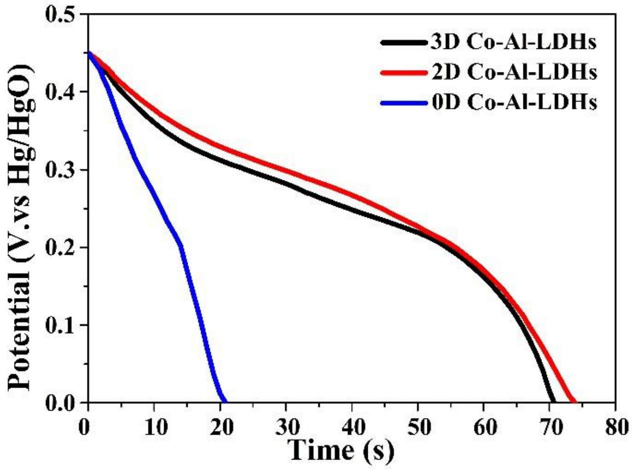


**Fig. S6** Galvanostatic charge-discharge measurements of all LDHs at 5 A $g^{-1}$

**Table S1** Comparison of the Csp, rate capability and cycle performances of our and the previous works

| **Electrodes based on materials** | **Csp ($F\cdot g^{-1}$)** | **Rate capability** | **cycle performances** | **Ref.** |
|---|---|---|---|---|
| **GSP/Co-Al-LDH** | 1043 (1 A $g^{-1}$ ) | 87% (20 A $g^{-1}$ ) | 3000 (88%, 100 mV $s^{-1}$) | [1] |
| **Co-Al-LDH** | 756 (1 A $g^{-1}$ ) | 44% (20 A $g^{-1}$ ) | 3000 (74%, 100 mV $s^{-1}$) | |
| **Co-Al LDH/CNT** | 884 (0.86 A $g^{-1}$ ) | 60% (4.3 A $g^{-1}$) | 2000 (88%, 1.72 A $g^{-1}$) | [2] |
| **Co-Al LDH** | 550 (0.86 A $g^{-1}$ ) | 51% (4.3 A $g^{-1}$) | 2000 (68%, 1.72 A $g^{-1}$) | |
| **Co-Al LDH/GNS** | 771 (1 A $g^{-1}$ ) | 73.2% (10 A $g^{-1}$ ) | 2000 (81%, 10 A $g^{-1}$ ) | [3] |
| **Co-Al LDH** | 641 (1 A $g^{-1}$ ) | 65.7% (10 A $g^{-1}$) | 2000 (64%, 10 A $g^{-1}$ ) | |
| **Co-Al LDH/GO** | 780 (1 A $g^{-1}$ ) | 80% (20 A $g^{-1}$ ) | 10000 (73%, 6 A $g^{-1}$ ) | [4] |
| **Co-Al LDH** | 701 (1 A $g^{-1}$ ) | 53% (20 A $g^{-1}$) | 10000 (52%, 6 A $g^{-1}$ ) | |
| **Co-Al LDH/rGO** | 621 (1 A $g^{-1}$ ) | 65% (8 A $g^{-1}$ ) | 5000 (92%, 4 A $g^{-1}$ ) | [5] |
| **Co-Al LDH** | 340 (2 A $g^{-1}$ ) | | | |
| **LDH/Ni foil** | 1031 (1 A $g^{-1}$ ) | 66% (100 A $g^{-1}$ ) | 2000 (92%, 4A $g^{-1}$ ) | [6] |
| **3D Co-Al-LDHs** | 838 (1 A $g^{-1}$ ) | 81% (100 A $g^{-1}$ ) | 20000 (95%, 5A $g^{-1}$ ) | This work |

GNS: graphene nanosheets
rGO: reduced graphene oxide
CNT: carbon nanotube
GSP: graphene sheets

**Table S2** Specific surface area and total pore volume of different samples

| **Sample** | **3D Co-Al-LDHs** | **2D Co-Al-LDHs** | **0D Co-Al-LDHs** |
|---|---|---|---|
| **Specific surface area ($m^2$ $g^{-1}$)** | 152 $m^2$ $g^{-1}$ | 90 $m^2$ $g^{-1}$ | 69 $m^2$ $g^{-1}$ |
| **Total pore volume ($cm^3$ $g^{-1}$)** | 0.53 $cm^3$ $g^{-1}$ | 0.19 $cm^3$ $g^{-1}$ | 0.25 $cm^3$ $g^{-1}$ |

3D hierarchical Co-Al-LDHs are composed of atomically thin nanosheets, which is extremely thin (0.8-1.6 nm) than 2D Co-Al-LDHs (~3 nm). Thus, the surface area of 3D hierarchical Co-Al-LDHs twice of 2D Co-Al-LDH. While the 0D Co-Al-LDHs solid nanospheres with some nanosheets on their surface, and result the smallest surface area.

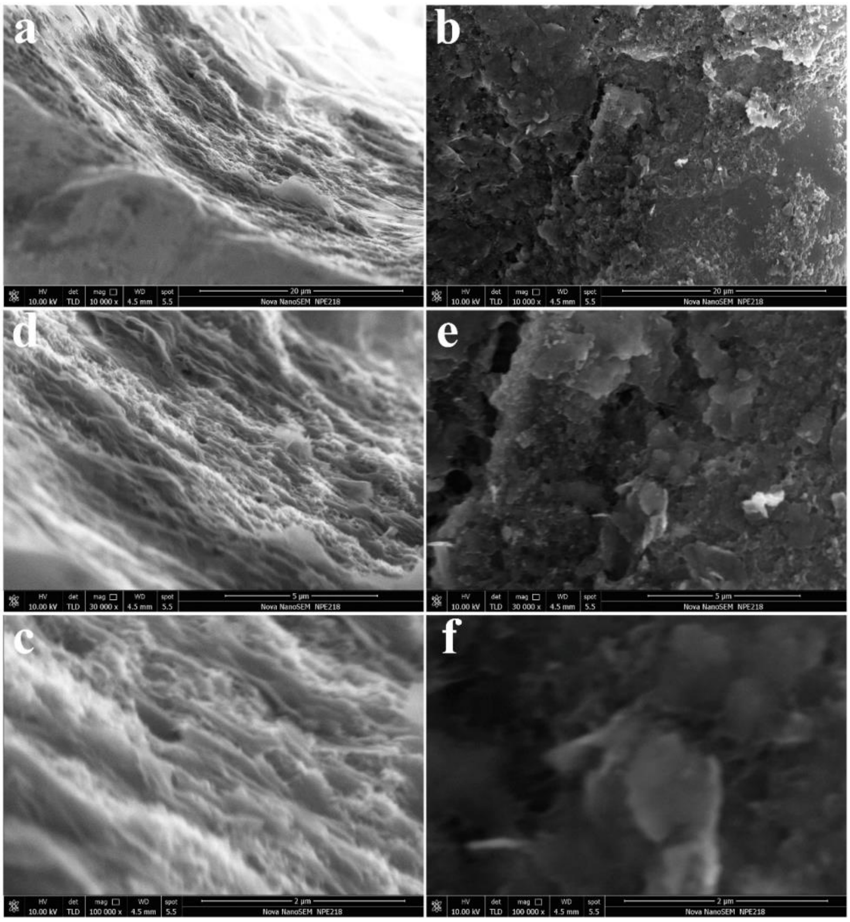


**Fig. S7** SEM images of fresh (**a-c**) and cycled (**e-f**) electrodes of 2D Co-Al-LDHs

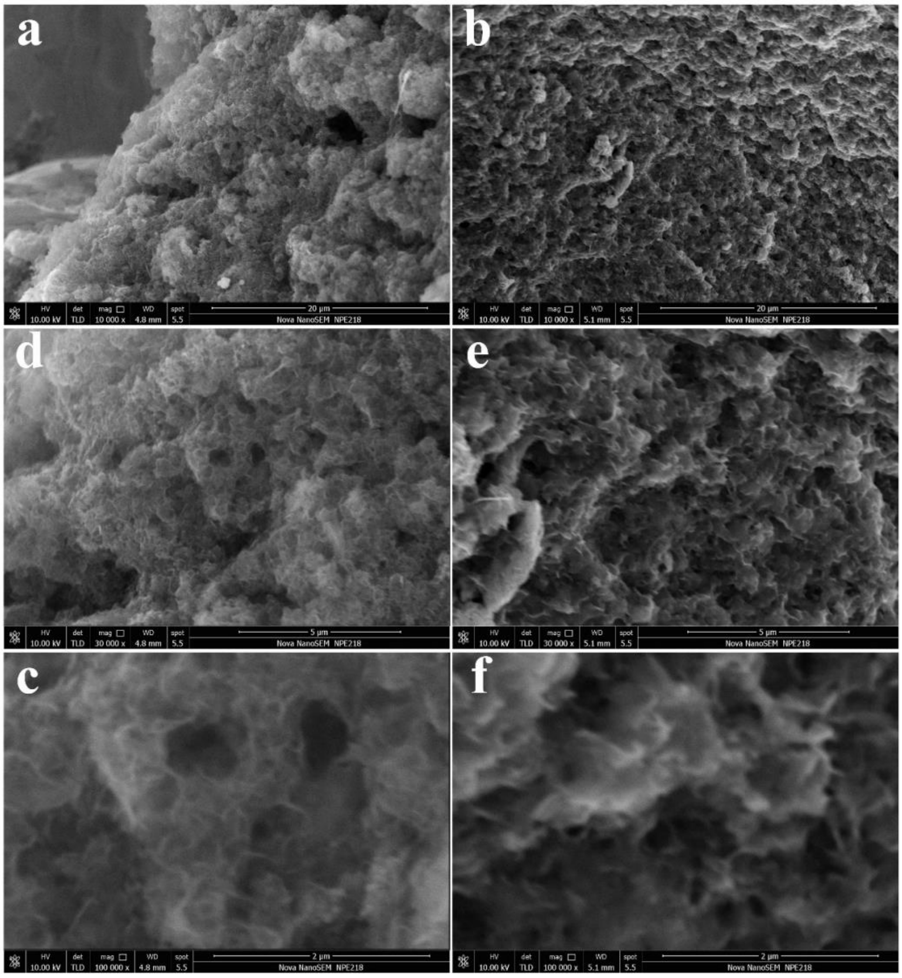

**Fig. S8** SEM images of fresh (**a-c**) and cycled (**e-f**) electrodes of 3D Co-Al-LDHs

The fresh 2D Co-Al-LDHs electrode is composed of loosely stacking nanosheets, which is benefit for the diffusion of electrolyte. However, these nanosheets become tightly stacking nanoplates after cycling, which would be the reason of capacity fading. Different from the 2D Co-Al-LDHs nanosheets, no obvious morphology changes can be observed in the 3D Co-Al-LDHs electrode after cycling. This result further confirms that the hierarchical structures built by ultrathin nanosheets can effectively prevent the stacking of nanosheets and stabilize the overall structures, which is important to the cycling stability.

## References

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