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# **Supporting Information**

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Interconnected Nanorods–Nanoflakes Li<sub>2</sub>Co<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> Framework Structure with Enhanced Electrochemical Properties for Supercapacitors

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### Supporting Information

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#### **Experimental Methods**

#### Interconnected nanorods-nanoflakes Li<sub>2</sub>Co<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> synthesis

All chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) and used as received without any further purification. Firstly, three dimensional (3D) pieces of nickel foam (0.2 mm  $\times$  20 mm  $\times$  50 mm in size) were cleaned with diluted nitric acid, ethanol and double distilled ionized (DDI) water prior to being used as substrate to support our synthesized materials. The  $Li_2Co_2(MoO_4)_3$  were synthesized by employing a mild hydrothermal method. For a typical synthesis, 0.34 g LiCl·H<sub>2</sub>O and 1.024 g CoCl<sub>2</sub>·6H<sub>2</sub>O were mixed and left to age for 24 hours. The as-obtained precursor was then dissolved in 30 ml DDI water and stirred for 1 hour. To this solution, an aqueous solution of 1.4 g Na<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O in 20 ml DDI water was drop wise added and the mixture was stirred for two hours. There was no precipitate observed during this step. However, to obtain Li<sub>2</sub>Co<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> grown on substrate, the as-prepared precursor was transferred into 100 ml autoclave containing the pretreated substrate then heated in an oven maintained at 120 °C for 12 hours and then left to cool down naturally at room temperature. The substrate supporting the as-synthesized product was removed from the autoclave and ultrasonically cleaned at 40 kHz for 5 minutes to remove the excess and not well attached materials, then rinsed several times with DDI water, before being vacuum-dried in the oven at 70 °C overnight. The as-obtained material was calcined in the air at 350 oC for one hour with a heating rate of 5 °C/min and left to cool down naturally after the annealing process.

#### **Reduced Graphene Oxide film synthesis method**

The Reduced Graphene Oxide film was synthesized following the method reported in reference.<sup>[1]</sup> For typical synthesis, a 100 ml solution of 0.5 mg/ml graphene oxide obtained through Hummers'modified method was mixed with 0.2 hydrazine hydrate (35 wt%) and 0.35 ml ammonia liquid (28 wt%) solution in beaker. After vigorous magnetic agitation for 20 minutes, the beaker was put in water bath at 100 °C for 3 hours. The film was obtained by vacuum filtration of the 40 ml solution of the as-prepared through a cellulose membrane (0.20  $\mu$ m pore size). The hydrogel films were carefully peeled off from the filter membrane, then immersed in DDI water for two days to further remove the remaining hydrazine and

ammonia. The as obtained films were around 5  $mg/cm^2$  and after removed from DDI, the film was immersed in the electrolyte solution overnight before to perform the electrochemical test.

#### Energy density and average power density calculation

The energy density and the average power density were determinate for full cell asymmetric supercapacitor in two electrodes technic according to following formulas<sup>[2]</sup>:

$$E = \frac{1}{2}CV^2 \qquad (1)$$
$$P_a = \frac{E}{\Delta t} \qquad (2)$$

Where *E* represent the energy density, *C*, the capacitance and *V*, the operating voltage while for the second formula  $P_a$  and  $\Delta t$  stand for average power density and discharge time, respectively. Obviously with the increase of the operating voltage the energy density is increase greatly, and asymmetric supercapacitors (ASCs) have demonstrated the increase of the operating voltage to high value in aqueous electrolyte without water decomposition.

For asymmetric supercapacitors (ASCs), the balance between the masses of the anode and cathode are expressed by the following equation<sup>[3]</sup>:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \tag{3}$$

where  $m_+$  and  $m_-$  represent the masses,  $C_+$  and  $C_-$ , the specific capacitance and  $\Delta V_+$  and  $\Delta V_-$ , the potential windows for the positive and negative electrode, respectively.



**Figure S1:** a) XRD spectrum of  $Li_2Co_2(MoO_4)_3$  before and after annealing process at different temperature. b) TEM image of a single nanorods with nanoflakes and (c,d) HRTEM images with the inset displaying the SEAD patterns of nanoflake and nanorods respectively, of the  $Li_2Co_2(MoO_4)_3$  calcined at 350 °C



**Figure S2**: Morphology evolution versus synthesis time; (a-d) scanning electronic microscopic images of the  $Li_2Co_2(MoO_4)_3$  after 4, 8, 12 and 16 hours reaction time on nickel foam, respectively. (e,f) SEM image of grown on carbon cloth and carbon fiber paper collected after 8 hours reaction time.



**Figure S3:** (a-d)SEM images of the  $Li_2Co_2(MoO_4)_3$  annealed at 350; 450; 550 and 650 °C, respectively in the air for 1 hour



**Figure S4:** (a,b) CV curves of  $Li_2Co_2(MoO_4)_3$  samples before and after calcination at 350 °C for a sweep rate range between 1 to 10 mV/s. CV curves collected at 10 mV/s (c) and galvanostatic charge-discharge graph at 1 A/g (d) for  $Li_2Co_2(MoO_4)_3$  annealed at 350 °C in LiOH, NaOH and KOH, respectively.

#### 5. In situ XDR measurements

For the in situ XRD, the testing cell was assembled with a cathode material composed by the  $Li_2Co_2(MoO_4)_3$  annealed at 350 °C, acetylene black and poly(tetrafluoroethylene) (PTFE) in the proportion of 7:2:1 wt%, acting as active material, conductive material and binder, respectively. The anode was constituted of pieces of carbon fiber paper (CFP) while the electrolyte was a 2 M aqueous solution of LiOH and KOH.



**Figure S5:** In situ XRD spectrum for  $Li_2Co_2(MoO_4)_3$  annealed at 350 °C in (a,b) LiOH and (c,d) KOH, respectively.



**Figure S6**: a) FTIR curves and b) SEM image of the as synthesized reduced graphene oxide film



**Figure S7:** a) CV curves, b) galvanostatic charge-discharge curves and c) rate capability of the reduced graphene oxide film (RGO) in 2 M LiOH aqueous electrolyte.

#### References

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