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Supporting information:

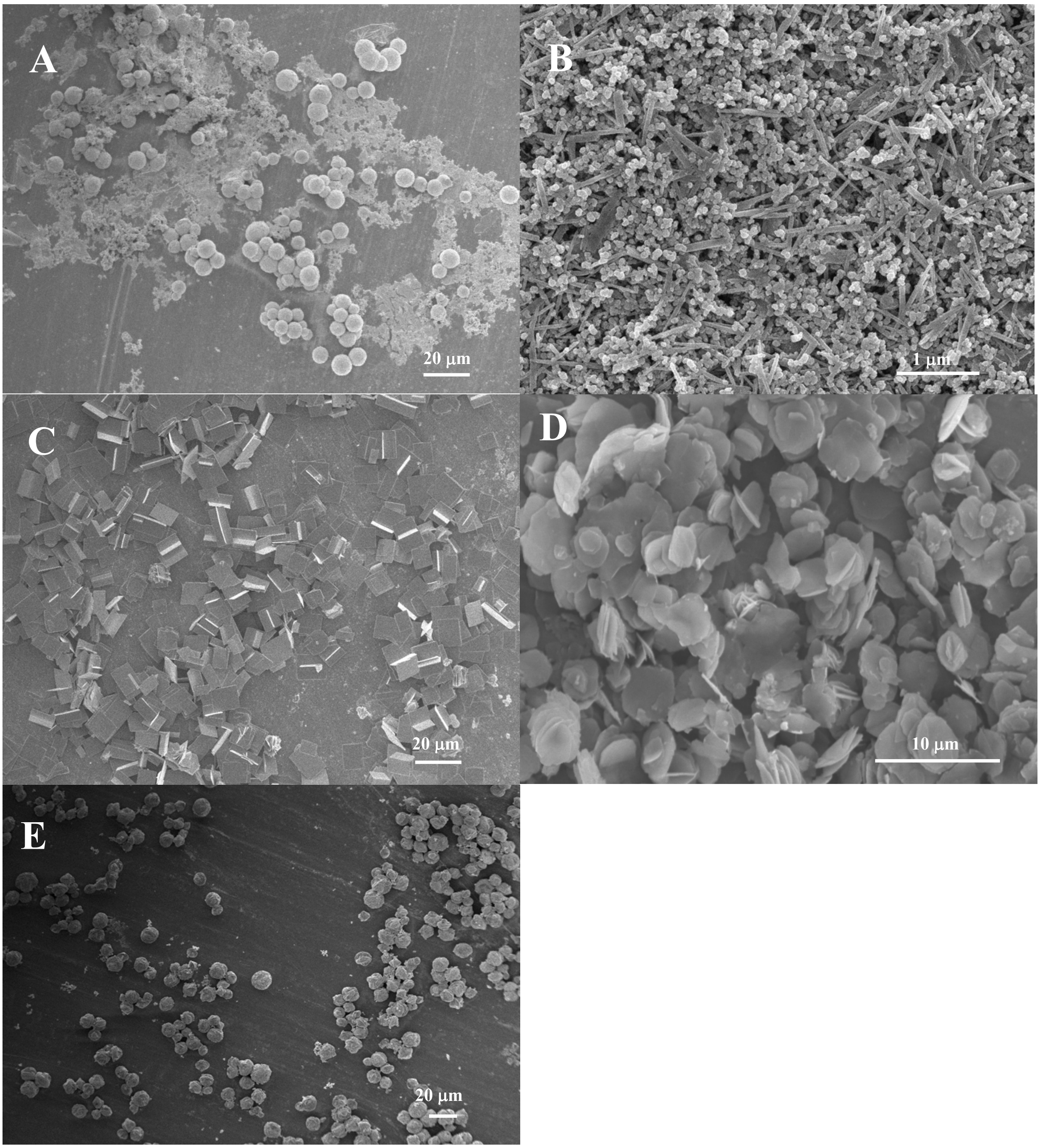

Figure S1 Low magnification SEM images of hierarchical VO*x* with (A) 0%, (B) 12.5 %, (C) 25 %, (D) 75 % and (E) 95 % water content.

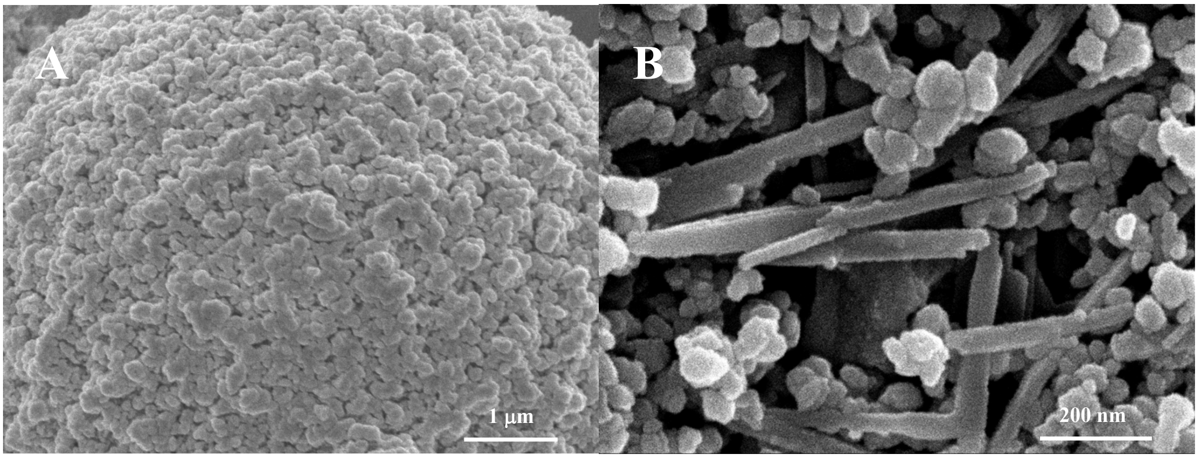

Figure S2 High magnification SEM images of hierarchical VO*x* with (A) 0% and (B) 12.5 % water content.

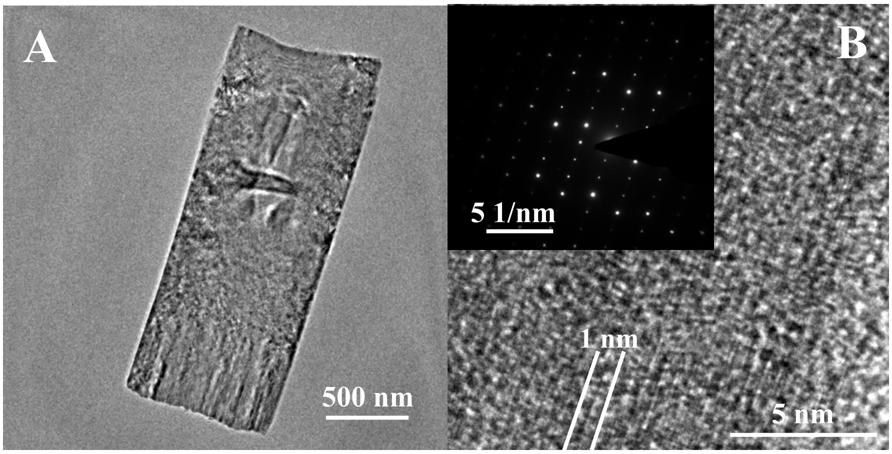

Figure S3 TEM images of V_4O_7 “nanocross” with (A) low resolution TEM image; (B) high resolution TEM image and SAED pattern inset.

The additional crystal phase between (001) may be derived from the shear plane of unique V_4O_7 crystallinity, which has “Zigzaged” layered structure. The SAED pattern (Fig. S3B inset) indicated a single-crystallized structure.

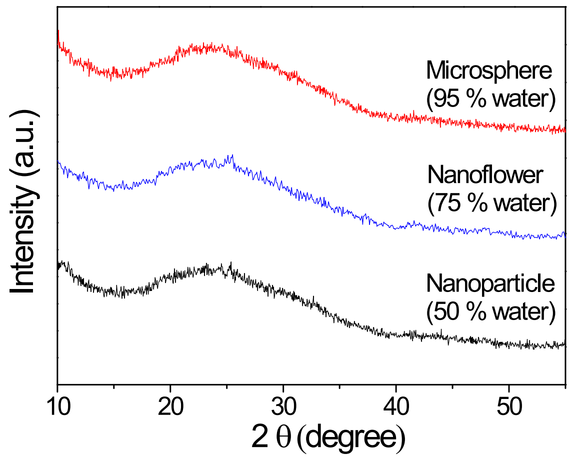

Figure S4 Crystallinity characterization of VO_x hierarchical structure with 50 %, 75 % and 95% water content.

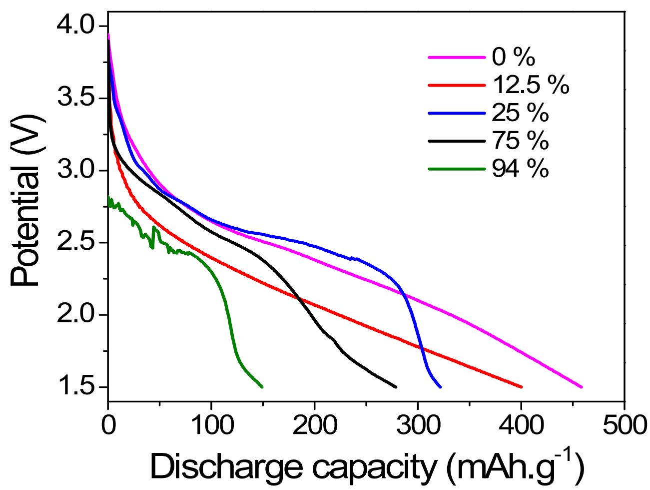

Figure S5 Corresponding discharge profiles of the initial cycle of VO_x hierarchical structures.

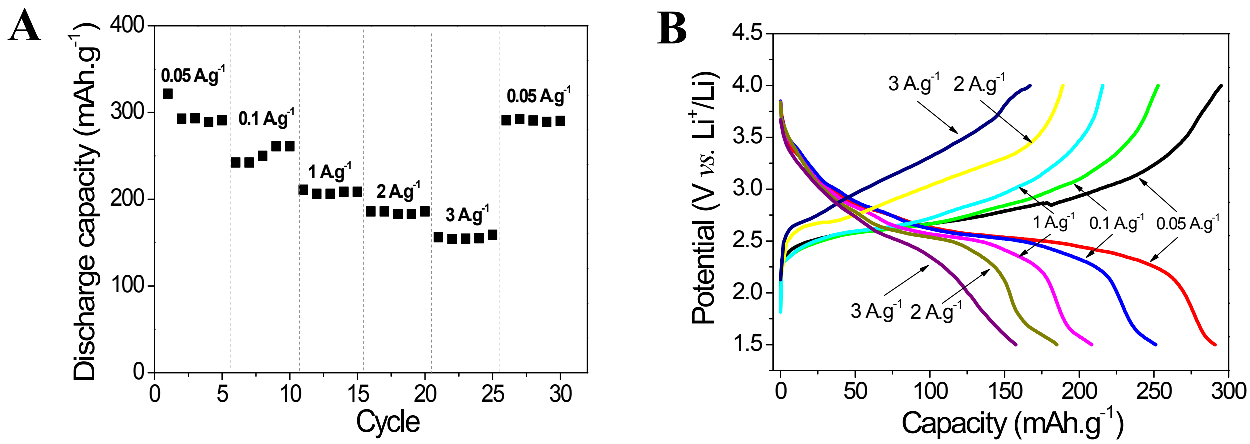

Figure S6 Rate performance of “nanocross” V_4O_7 with (A) different current density and (B) corresponding charge/discharge profile.

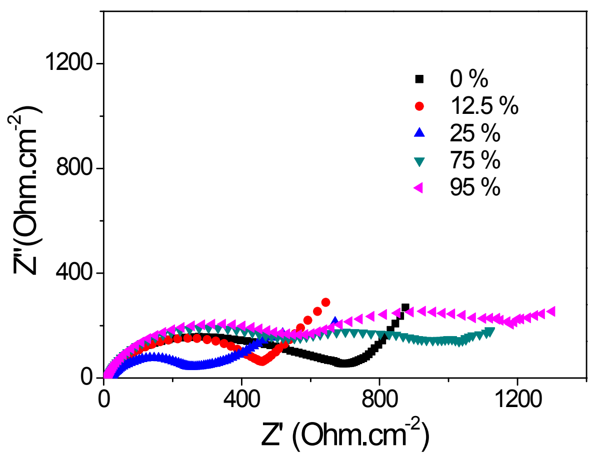

Figure S7 EIS tests of hierarchical VOx with different water content after 100 cycles at 0.05 $A.g^{-1}$.

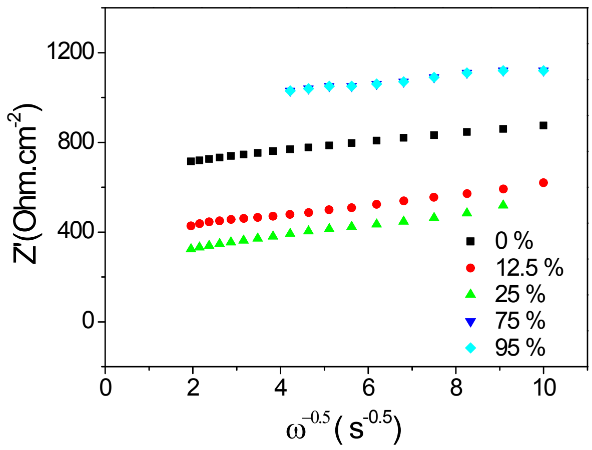

Figure S8 Comparison of Z'-$\omega^{-0.5}$ plot of hierarchical VOx with different water content.

Warburg coefficient σ_w calculation: The EIS spectrum is composed of a semicircle at high frequency and a linear line within the low frequency. The diameter of the semicircle represents the resistance of the charge transfer process and the slope of the linear line corresponds with the lithium ions diffusion into the bulk of the electrode, the Warburg diffusion. The Warburg coefficient σ_w can be obtained by Equation (2):

$$Z_{re} = R_e + R_{ct} + \sigma_w \omega^{-0.5} \qquad (1)$$

where R_e is the electrolyte resistance, R_{ct} is the electron transfer resistance and ω is the angular frequency which is quantitatively calculated by the frequency within the measurement range of 0.1 Hz to 100 kHz. Therefore, σ_w is the slope for the Z_{re} *vs.* $\omega^{-0.5}$ plot.

Diffusion coefficient *D* calculation:

$$D = 0.5\left(\frac{RT}{AF^2\sigma_w C}\right) \qquad (2)$$

where R is the gas constant, T is the measurement temperature, A is the area of the electrode surface, F is the Faraday's constant and C is the concentration of lithium ions.

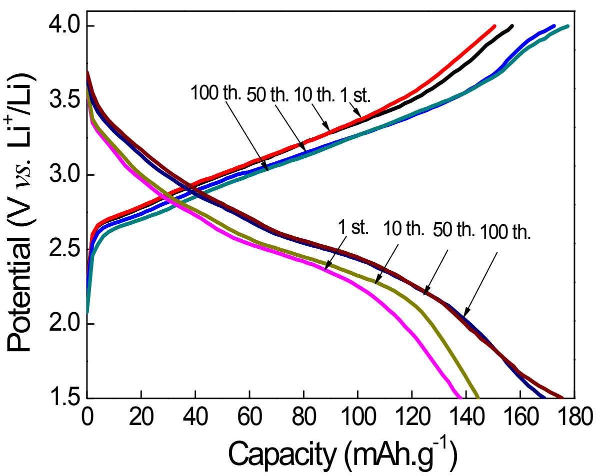

Figure S9 The corresponding charge/discharge profile of "nanocross" cycled at 3.05 A.g^{-1}.