

**Electronic Supplementary Information**

**Tuning pseudocapacitive and battery-like lithium  
intercalation in vanadium dioxide/carbon onion  
hybrids for asymmetric supercapacitor anodes**

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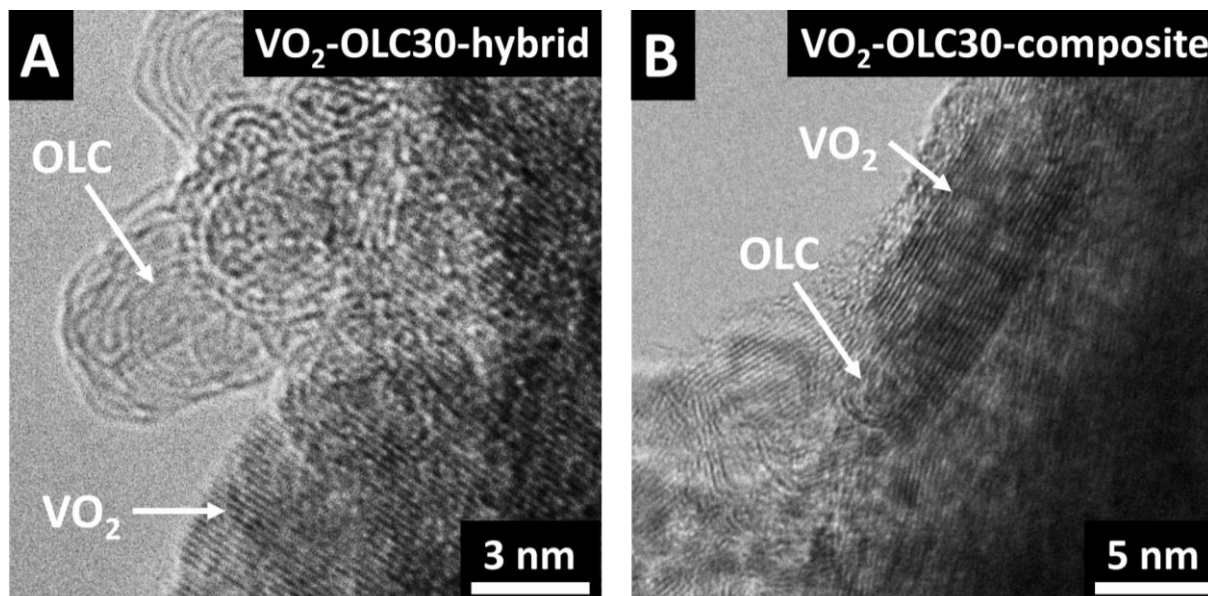
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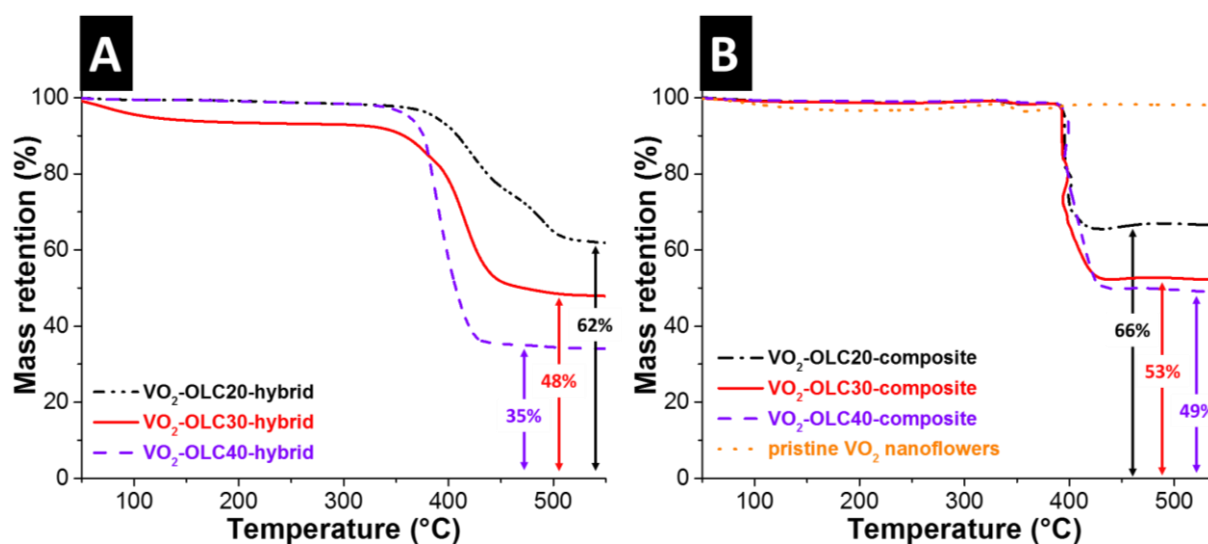
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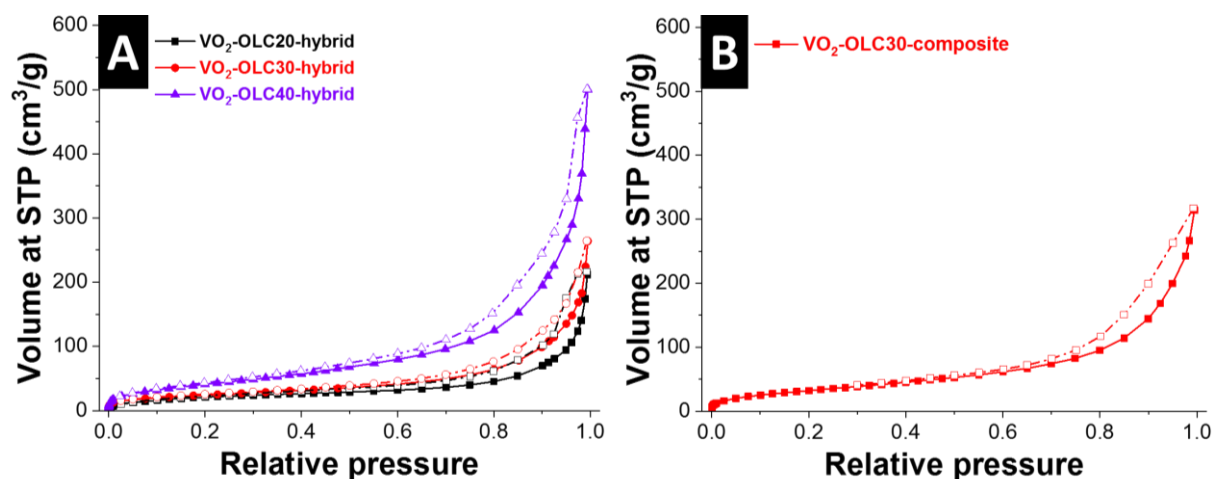
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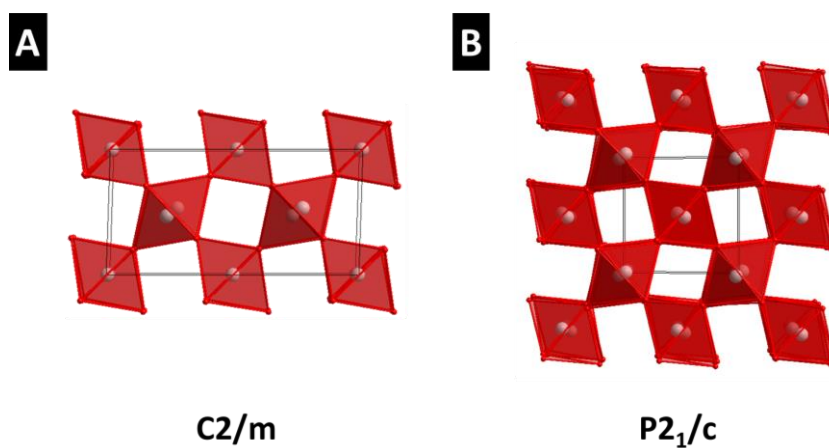
**Figure S1:** Transmission electron micrographs of (A) VO<sub>2</sub>-OLC30-hybrid and (B) VO<sub>2</sub>-OLC30-composite samples.



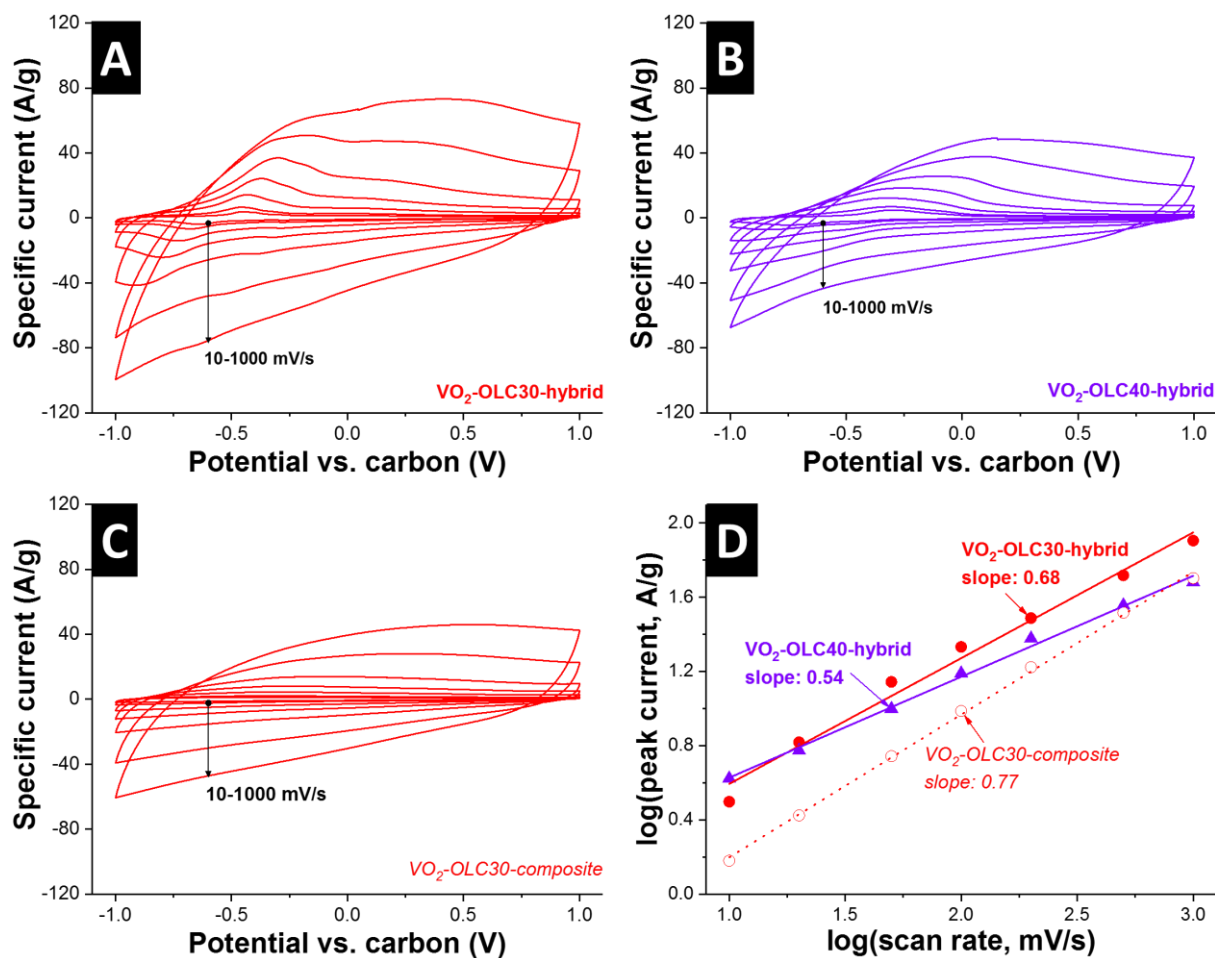
**Figure S2:** Thermogravimetric analysis of (A) VO<sub>2</sub>-OLC-hybrid samples and (B) VO<sub>2</sub>-OLC-composite samples and pristine VO<sub>2</sub> nanoflowers, carried out in synthetic air (flow rate of 20 mL·min<sup>-1</sup>) up to a temperature of 550 °C at a heating rate of 5 °C·min<sup>-1</sup>.



**Figure S3:** Nitrogen sorption isotherms at standard temperature and pressure of (A) VO<sub>2</sub>-OLC-hybrid samples and (B) VO<sub>2</sub>-OLC30-composite sample. The dashed lines correspond to the desorption branch.



**Figure S4:** Crystal structures of the monoclinic VO<sub>2</sub> structure in (A) C2/m and (B) P2<sub>1</sub>/c space group. The vanadium atoms are represented by white spheres, oxygen atoms by red spheres. The distances between the shared oxygen atoms at the corners of the octahedra show a fixed distance of 3.3 Å for C2/m and a varying distance between 2.9 Å and 6.4 Å for P2<sub>1</sub>/c.



**Figure S5:** CVs of (A) VO<sub>2</sub>-OLC30-hybrid, (B) VO<sub>2</sub>-OLC40-hybrid, and (C) VO<sub>2</sub>-OLC30-composite samples measured in half-cells and varying scanning speeds of 10-1000 mV·s<sup>-1</sup>. (D) Kinetic analysis via logarithmic plotting of the peak current at -0.7 V vs. carbon against the scan rate and linear regression applied to the data points.

**Table S1:** Electrode conductivity of VO<sub>2</sub>-OLC30-hybrid and VO<sub>2</sub>-OLC30-composite electrodes by 4-point probe as an average of six measurements.

Material	Electrode conductivity (S·cm <sup>-1</sup> )
VO <sub>2</sub> -OLC30-hybrid	0.30 ± 0.03
VO <sub>2</sub> -OLC30-composite	0.16 ± 0.05

**Table S2:** Specific surface area (BET) and pore volume (at P/P<sub>0</sub>=0.95) of VO<sub>2</sub>-OLC samples and as synthesized vanadium oxide nanoflowers and carbon onions.

Material	SSA (BET) (m <sup>2</sup> ·g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> ·g <sup>-1</sup> )
VO <sub>2</sub> -OLC20-hybrid	81	0.15
VO <sub>2</sub> -OLC30-hybrid	89	0.21
VO <sub>2</sub> -OLC40-hybrid	160	0.41
VO <sub>2</sub> -OLC30-composite	118	0.31
VO <sub>2</sub> as synthesized	38	0.04
OLCs as synthesized	352	0.93

**Table S3:** Analysis of D- and G-bands of the samples VO<sub>2</sub>-OLC30-hybrid and VO<sub>2</sub>-OLC30-composite, calculated by peak deconvolution.

Material	FWHM D (cm <sup>-1</sup> )	FWHM G (cm <sup>-1</sup> )	I <sub>D</sub> /I <sub>G</sub>	Pos. D-band (cm <sup>-1</sup> )	Pos. G-band (cm <sup>-1</sup> )
VO <sub>2</sub> -OLC30-hybrid	69	48	2.7	1347	1590
VO <sub>2</sub> -OLC30-composite	58	40	2.3	1347	1587