Electronic Supplementary Information

A Li-Rich Layered@Spinel@Carbon Heterostructured Cathode Material for High Capacity and High Rate Li-Ion Batteries Fabricated *via* an *in situ* Synchronous Carbonization-Reduction Method

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Scheme S1 Schematic diagrams for design and synthesis of the Layered@Spinel@Carbon heterostructure.



Fig. S1 HRTEM images of L@S@C-2 and L@S@C-3.



Fig. S2 Scheme of layered-to-spinel structural transformation.

Table S1 The comparative data of initial discharge capacities and corresponding coulombicefficiency of Li-rich layered oxide materials at room temperature between 2.0 V and 4.8 V

Ref.	Current	Discharge Capacity	Coulombic Efficiency	
	mA g⁻¹	mAh g⁻¹	%	
[1]	10	287	87.5	
[2]	20	~250	Unknown	
[3]	25	~300	Unknown	
[4]	5	299	88	
[5]	40	276.4	87.7	
[6]	20	300.3	84.4	
[7]	12.5	298	88.2	
[8]	12.5	273	78.7	
This work	25	334.5	92.2	

from different researches.



Fig. S3 Cycling performance of the pristine and heterostructured samples at 0.2 C.



Fig. S4 Charge/discharge curves for pristine (a) and L@S@C-1 (b) samples for 1st, 10th, 20th, 30th, 40th, 50th and 60th cycles. (c) and (d) Corresponding dQ/dV curves.

As shown in Figure S4a and c, the pristine sample shows a gradually voltage decay from the 1st cycle to the 60th cycle, due to the continuous layered-to-spinel phase transformation. While the transformation ceased after 30 cycles for the L@S@C-1 sample (Figure S4b and d), the peak around 3V did not change from the 30th cycle to the 60th cycle, suggesting better structural compatibility which can restrain further transformation. The ~2.7 V discharge plateaus associated with the interlayer spinel structure still exist even after 60 cycles (red box in Figure S4d). Both of carbon coating layer and the 3D framework of spinel interlayer are benefit to improve the stability of the layered bulk, to restrain the lattice rearrangement during cycle process, enhancing the cycle performance.



Fig. S5 Discharge curves for L@S@C-2 (a) and L@S@C-3 (b) at different C-rates. (c) and (d) Discharge voltage profiles of both pristine and heterostructured samples at discharge rates of 20 C and 30 C (0.1 C charge rate), respectively.

Table S2 Discharge capacities of both pristine and heterostructured samples at different C-rates after being charged to 4.8 V at 0.1 C.

Rate	Pristine (mAh g ⁻¹)	L@S@C-1 (mAh g ⁻¹)	L@S@C-2 (mAh g ⁻¹)	L@S@C-3 (mAh g⁻¹)
1C	241.7	275.9	268.7	200
2C	208.4	273.2	257.9	185.6
4C	187.4	243.7	245.4	171.9
6C	163.4	245	231.4	160.2
10C	73.6	233.7	215.1	144.3
20C	98.5	162.4	149.9	112.4
30C	55.3	122.7	76.2	67.8



Fig. S6 (a) and (b) Cycling performance of L@S@C-2 and L@S@C-3 at different discharge rates (0.1 C charge rate). (c) and (d) Charge/discharge rate performance of L@S@C-2 and L@S@C-3 after two activation cycles at 0.1 C.

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