## **Supporting Information (SI)**

## LiAlH<sub>4</sub> supported on TiO<sub>2</sub>/hierarchically porous carbon

## nanocomposite with enhanced hydrogen storage properties†

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## Synthesis of hierarchically porous carbon (HPC)

In the process, 0.5g 2123# thermoplastic phenolic resin (Tianjin Letai Chemical Plant) was dissolved in 20 mL of absolute ethanol at 50 °C followed by adding 2 mL tetraethyl orthosilicate (TEOS) and stirred for 15 min until the solution became yellow and transparent. Then, 50mL 25wt% aqueous ammonia /ethanol mixture (volume ratio is 1:4) was rapidly poured into the solution under vigorous stirring. After a 3 h reaction at 50 °C, the solvent was gradually dried at 60 °C. The obtained yellow composite was calcined at 700 °C for 2 h in an Ar atmosphere. Subsequently, the black product was treated with 20 mL HF solution (10 wt%) to remove the silicon dioxide template and washed with distilled water, followed by drying at 80 °C in oven to get the product.



Fig. S1 Particle size analysis of TiO<sub>2</sub>/HPC nanocomposite with 40 wt% TiO<sub>2</sub>.



**Fig. S2** SEM images of TiO<sub>2</sub>/HPC nanocomposites with (a, b) 20 wt% TiO<sub>2</sub>, (c, d) 50 wt% TiO<sub>2</sub>, (e, f) 60 wt% TiO<sub>2</sub>.



Fig. S3 N2 adsorption/desorption curves of (a) HPC, (b) TiO2/HPC nanocomposite with 40 wt% TiO2, (c) 37LAH-

25TiO<sub>2</sub>/38HPC,

Samula	Surface area	total pore volume	Average pore	
Sample	(m <sup>2</sup> .g <sup>-1</sup> )	(cm <sup>3</sup> .g <sup>-1</sup> )	diameter (nm)	
НРС	412.55	0.3511	3.40	
TiO <sub>2</sub> /HPC with 40 wt% TiO <sub>2</sub>	254.21	0.2892	4.55	
37LAH-	22.14	0.0821	14.83	
25110 <sub>2</sub> /38HPC				

Table S1. Summary of BET specific surface area, total pore volume and average pore diameter.

The isotherm curves of HPC display a typical IUPAC type-IV adsorption/desorption behavior, indicating mesoporous structure. After supporting 40 wt% TiO<sub>2</sub> nanoparticles, the hysteresis in the isotherm of TiO<sub>2</sub>/HPC nonocomposite becomes smaller implying the decrease amount of mesopores and the surface area of TiO<sub>2</sub>/HPC is decreased to 254.21 m<sup>2</sup> g<sup>-1</sup>. The highly distribution of TiO<sub>2</sub> nanoparticles attributes to the large surface of HPC. Besides, plenty of pores would be favorable for the decomposition of LiAlH<sub>4</sub> by offering abundant channels for the diffusion of hydrogen.



Fig. S4 SEM images of (a) pure-LAH, (b) 29LAH-28TiO<sub>2</sub>/43HPC, (c) 45LAH-22TiO<sub>2</sub>/33HPC, (d) 55LAH-18TiO<sub>2</sub>/27HPC.

For pure LiAlH<sub>4</sub>, it is composed of monolith between 1-20 µm. In the sample 29LAH-

 $28\text{TiO}_2/43\text{HPC}$ , the TiO<sub>2</sub>/HPC was not completely coated by LiAlH<sub>4</sub> and the baked parts may not play the efficient role to facilitate the decomposition of LiAlH<sub>4</sub> without close contact. When increasing the loading weight of LiAlH<sub>4</sub> to 50, 60 wt%, the congregation of LiAlH<sub>4</sub> is more and more serious. This is unfavorable for reducing the dehydrogenation temperatures of LiAlH<sub>4</sub>.



**Fig. S5** FTIR spectra of (a) pure LAH and (b) 55LAH-18TiO<sub>2</sub>/27HPC, (c) 45LAH-22TiO<sub>2</sub>/33HPC, (d) 37LAH-25TiO<sub>2</sub>/38HPC, (e) 29LAH-28TiO<sub>2</sub>/43HPC composites after aging for 5 months at room temperature.



**Fig. S6** (a) SEM image of LAH-HPC, (b) SEM image of LAH-TiO<sub>2</sub>, (c) XRD patterns, (d) FTIR spectra and (e) TPD signal curves of LAH-HPC and LAH-TiO<sub>2</sub>.



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Fig. S7 The line chart of desorption temperatures.



Fig. S8 Hydrogen desorption kinetic curves of (a) pure-LAH, (b) LAH-TiO<sub>2</sub>, (c) LAH-HPC at different temperatures.

Pure	e-LAH	LA	H-TiO <sub>2</sub>	LAI	І-НРС	37LAH-25	TiO <sub>2</sub> /38HPC
T/°C	H <sub>2</sub> /wt%	T/°C	H <sub>2</sub> /wt%	T/°C	H <sub>2</sub> /wt%	T/°C	H <sub>2</sub> /wt%
150	3.34	145	3.86	145	4.28	100	2.30
160	5.30	160	5.55	160	5.57	110	3.07
178	5.31	170	5.87	170	6.61	120	3.67
188	5.46					130	4.32

**Table S2.** The dehydrogenation capacities (calculated from pure LiAlH<sub>4</sub>) of pure-LAH, LAH-HPC, LAH-TiO<sub>2</sub> and  $37LAH-25TiO_2/38HPC$  at various temperatures.

**Table S3.** The activation energy of pure-LAH, LAH-HPC, LAH-TiO<sub>2</sub> and 37LAH-25TiO<sub>2</sub>/38HPC according to Arrhenius plots.

samples				37LAH-
	Pure-LAH	LAH-IIO <sub>2</sub>	<b>LAH-НРС</b>	25TiO <sub>2</sub> /38HPC
Slope	-13.6	-6.97	-7.64	-5.7
Intercept	29.6	14.58	16.12	12.7
Ea (kJ/mol)	113.2±6.4	57.8±2.1	63.5±0.4	47.1±3.5



Fig. S9 The error bars for the Ea calculation of pure-LAH, LAH-HPC, LAH-TiO<sub>2</sub> and 37LAH-25TiO<sub>2</sub>/38HPC.



Fig. S10 SEM image and EDS elemental mapping images of 37LAH-25TiO<sub>2</sub>/38HPC after dehydrogenation.



Fig. S11 (a) SEM image and (b) TEM image of  $37LAH-25TiO_2/38HPC$  after re-adsorbing H<sub>2</sub> at 300 °C under a hydrogen pressure of 4 MPa.