Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Interface Controlled Solid-State Lithium Storage in Free-Standing Bismuth Nanosheets

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Table S1 Cyclability and rate capability comparison of bismuth anode materials in batteries with solid-state or liquid electrolytes and other reported representative works [S1-S6].

Anode material	Rate Capability (mAh g^{-1})	Cycling Capacity (mAh g^{-1})	Batteries	Ref.
Bismuth nanorod	~350.1 at 50 mA g^{-1} ~292.5 at 100 mA g^{-1} ~211.8 at 500 mA g^{-1} ~142.6 at 1000 mA g^{-1} ~102.3 at 2000 mA g^{-1}	~302 after 150 cycles at 50 mA g^{-1}	Sodium-ion batteries (Liquid)	[S1]
Bismuth bulk	~394.8 at 50 mA g^{-1} ~385.1 at 100 mA g^{-1} ~382.9 at 400 mA g^{-1} ~371.9 at 800 mA g^{-1} ~369.8 at 1200 mA g^{-1} ~362.9 at 1600 mA g^{-1} ~356.0 at 2000 mA g^{-1}	~389 after 2000 cycles at 400 mA g^{-1}	Sodium-ion batteries (Liquid)	[S2]
Bismuth nanoparticles@C	~260 at 100 mA g^{-1} ~220.1 at 200 mA g^{-1} ~178.8 at 500 mA g^{-1} ~130.4 at 1000 mA g^{-1} ~83.4 at 2000 mA g^{-1} ~160 at 100 mA g^{-1}	~123 after 100 cycles at 100 mA g^{-1}	Sodium-ion batteries (Liquid)	[S3]
Bismuth nanoparticles@C	~299 at 100 mA g^{-1} ~252 at 200 mA g^{-1} ~192 at 500 mA g^{-1} ~141 at 1000 mA g^{-1} ~90 at 2000 mA g^{-1} ~282 at 100 mA g^{-1}	~280 after 100 cycles at 100 mA g^{-1}	Lithium-ion batteries (Liquid)	[S3]
Bimuth@Graphite	~160 at 160 mA g^{-1} ~158 at 320 mA g^{-1} ~155 at 1600 mA g^{-1} ~156 at 1600 mA g^{-1}	~142 after 10000 cycles at 3200 mA g^{-1}	Sodium-ion batteries (Liquid)	[S4]
Bismuth nanoparticles	~350 at 17.5 mA g^{-1} ~342 at 70 mA g^{-1} ~329 at 175 mA g^{-1} ~319 at 350 mA g^{-1} ~313 at 700 mA g^{-1} ~216 at 1750 mA g^{-1}	~303 after 200 cycles at 700 mA g^{-1}	Magnesium-ion batteries (Liquid)	[S5]
$BiPO_4$@Graphite	/	~304 after 100 cycles at 50 mA g^{-1}	Lithium-ion batteries (Solid)	[S6]
Bismuth nanosheets	**~411 at 250 mA g^{-1}** **~364 at 500 mA g^{-1}** **~321 at 1000 mA g^{-1}** **~278 at 2000 mA g^{-1}** **~239 at 4000 mA g^{-1}** **~357 at 250 mA g^{-1}**	**~287 after 100 cycles at 250 mA g^{-1}**	**Lithium-ion batteries (Solid)**	**This work**

Table S2 Temperature-dependent lithium ionic conductivity of selected liquid or solid state electrolytes including hydrides and oxides compared with $LiPF_6$ liquid electrolyte.

Sample	30 ℃ (S cm^{-1})	90 ℃ (S cm^{-1})	120 ℃ (S cm^{-1})	Ref.
$LiPF_6$ liquid electrolyte	4.5×10^{-3}	/	/	[S7]
$Li(CB_9H_{10})_{0.7}(CB_{11}H_{12})_{0.3}$	6.7×10^{-3}	/	8.5×10^{-2}	[S8]
$Li_4(BH_4)(NH_2)_3$	3.1×10^{-4}	7.8×10^{-4}	1.1×10^{-3}	[S9]
$Li_7La_3Zr_2O_{12}$	1.6×10^{-6}	7.1×10^{-4}	/	[S10]
Li_3PO_4	4.1×10^{-8}	/	/	[S11]
$LiBH_4$	**1.5×10^{-8}**	**1.4×10^{-6}**	**1.5×10^{-3}**	[S12]
LiI	3.2×10^{-8}	5.2×10^{-7}	1.4×10^{-6}	[S13]
$LiNH_2$	/	2.5×10^{-7}	2.5×10^{-6}	[S13]
$LiAlH_4$	8.7×10^{-9}	3.6×10^{-6}	1.5×10^{-5}	[S14]
$LiBH_4 \cdot 0.5NH_3$	1.0×10^{-4}	4.0×10^{-2}	/	[S15]

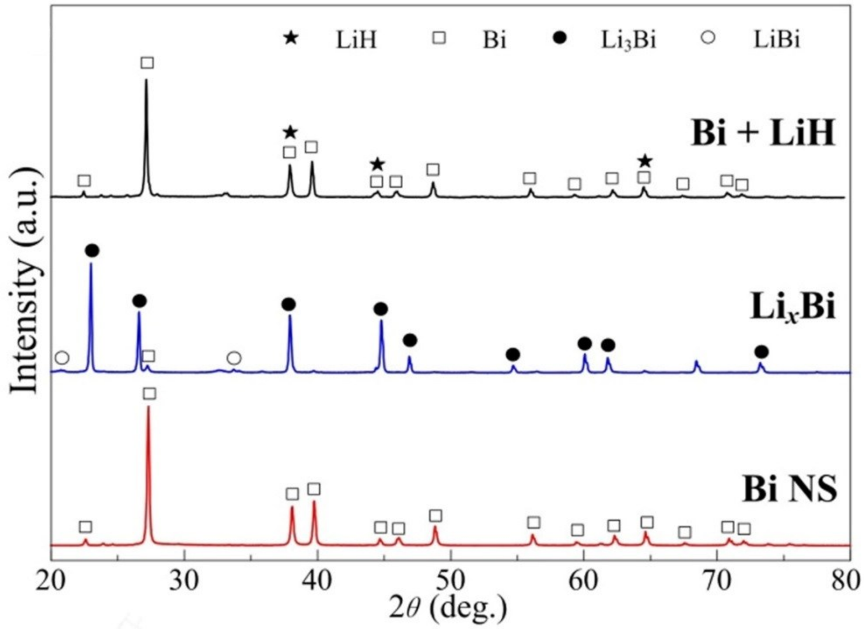

Figure S1 XRD patterns for the Li-Bi system at different stages of the synthesis.

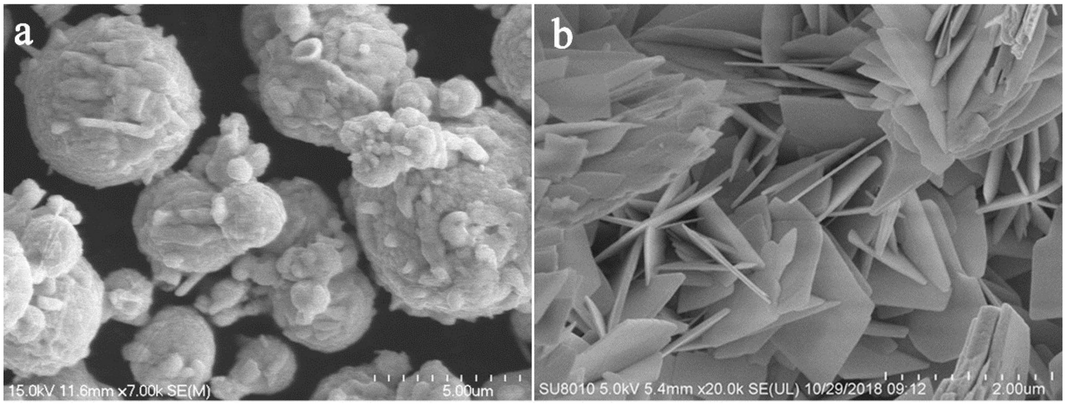

Figure S2 SEM images of the a) Bulk-Bi micro-spheres and b) Bi-NSs nanosheets.

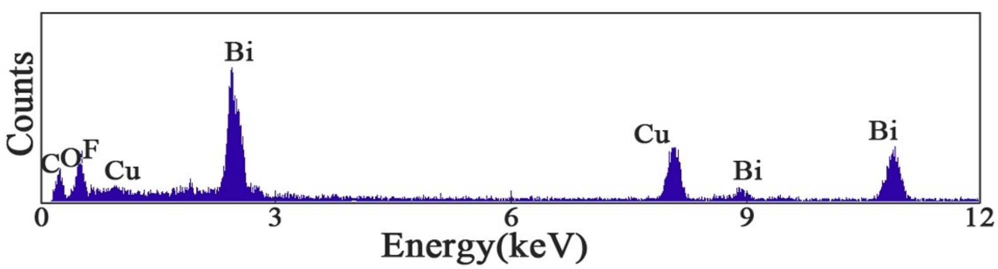

Figure S3 Energy dispersive spectroscopy (EDS) of Bi-NSs electrode material after 100th lithiation /delithiation cycles at 250 mA g^{-1}.

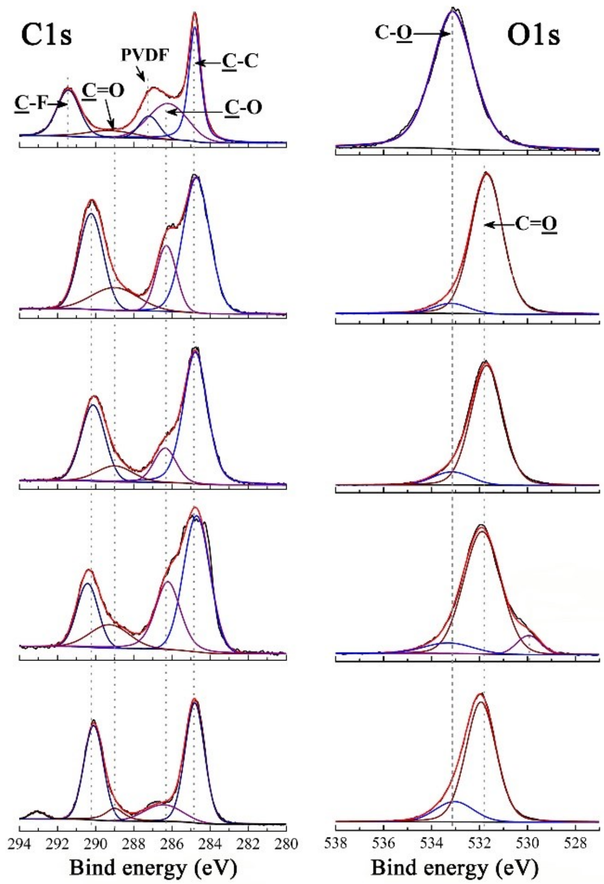

Figure S4 C1s and O1s XPS spectra for the Bi-NSs samples upon lithiation/delithiation corresponding to Figure 2c.

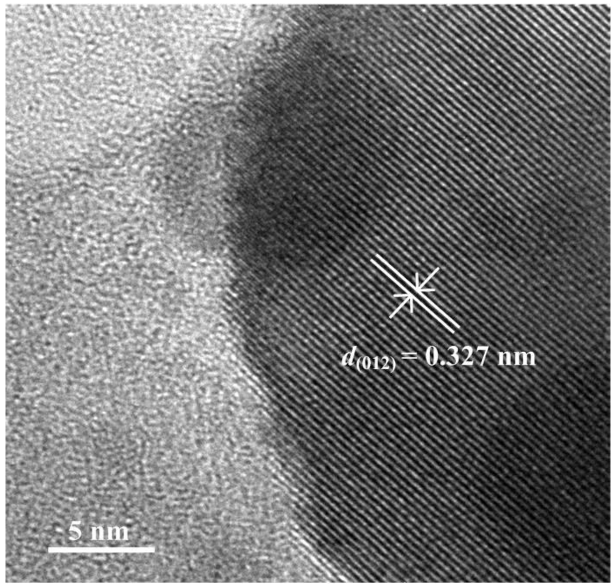

Figure S5 HRTEM image for the cyclic Bi-NSs anode.

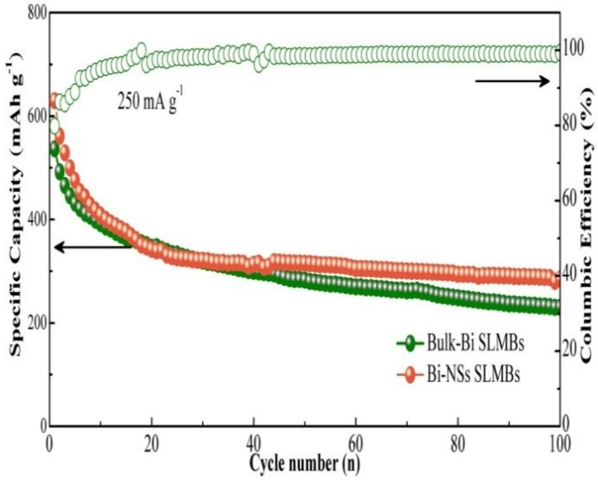

Figure S6 Cycling performances of different Bi anodes in solid-state LIBs with half-cell structure.

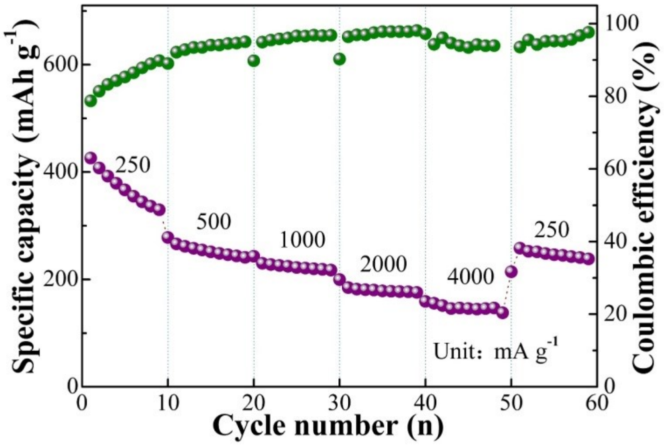

Figure S7 Rate capabilities of Bulk-Bi half-cells at various current densities from 250 to 4000 mA g^{-1}.

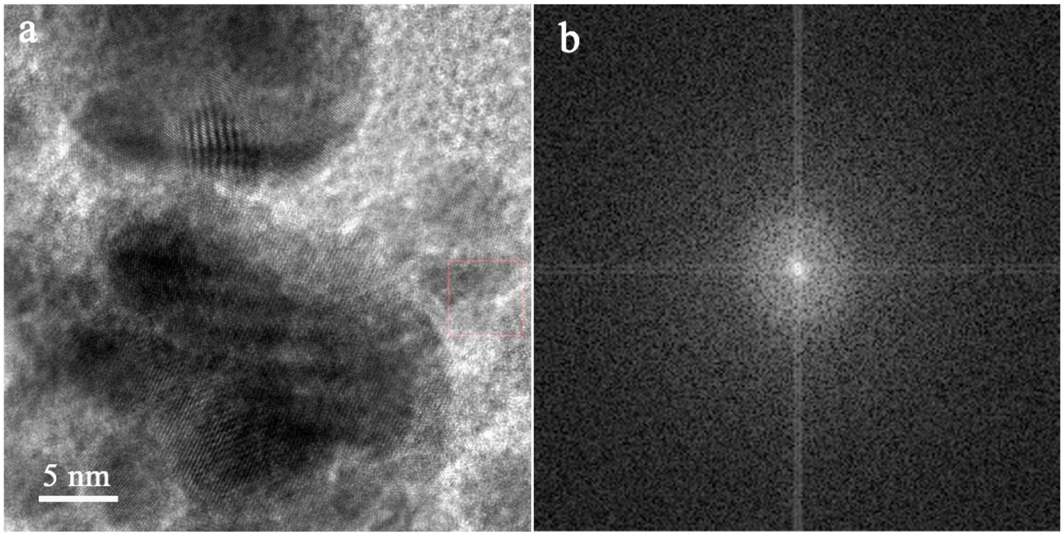

Figure S8 a) HRTEM images for discharge state of Bi-NSs electrode; b) FFT digital diffractogram image of the $LiBH_4$ inside the pink box in a).

Supplementary References

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