Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Ultra-fine Surface Solid-State Electrolyte for Long Cycle Life All-Solid-State Lithium-Air Battery

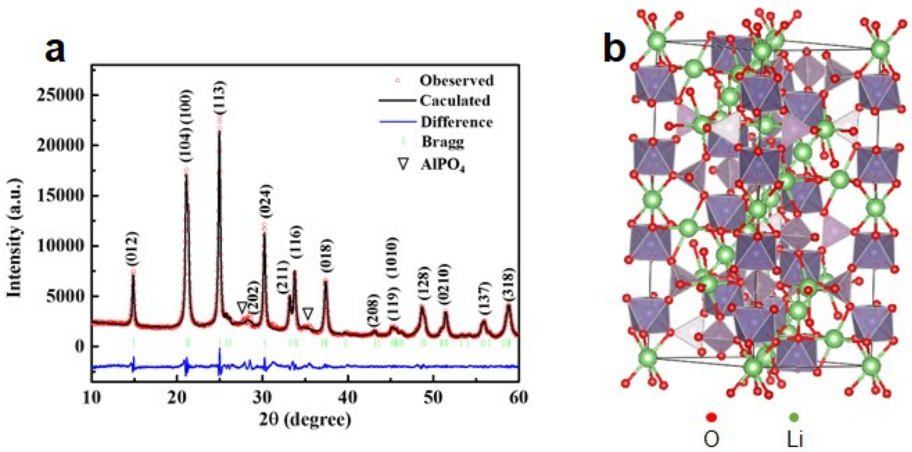

Figure S1 a) The X-ray diffraction pattern (XRD) characterization of LAGP electrolyte. b) Crystal structure of NASICON-type LAGP. The prepared LAGP has a rhombohedral structure with space group *R*3*c*, and an open three-dimensional framework sharing all corners of GeO_6 octahedra with PO_4 tetrahedra.

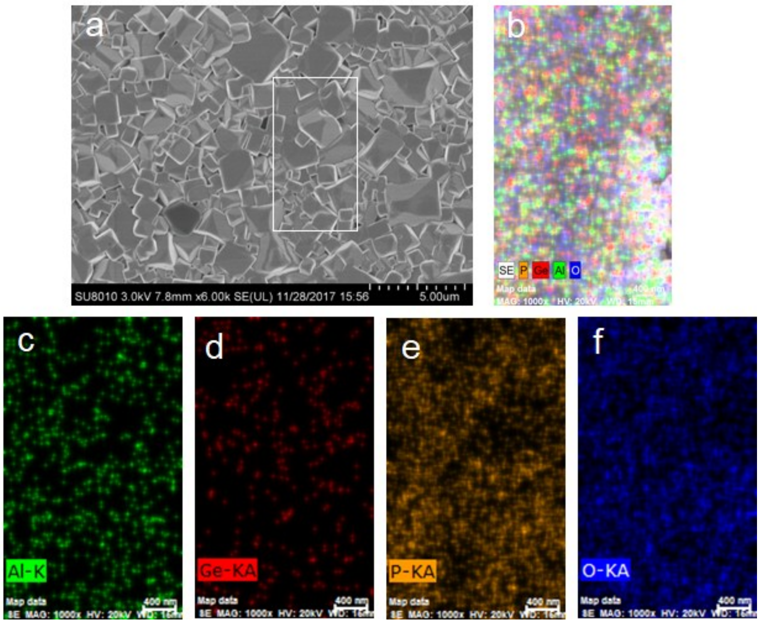

Figure S2 (a) SEM image and (b-f) EDS mapping of LAGP with protrusions.

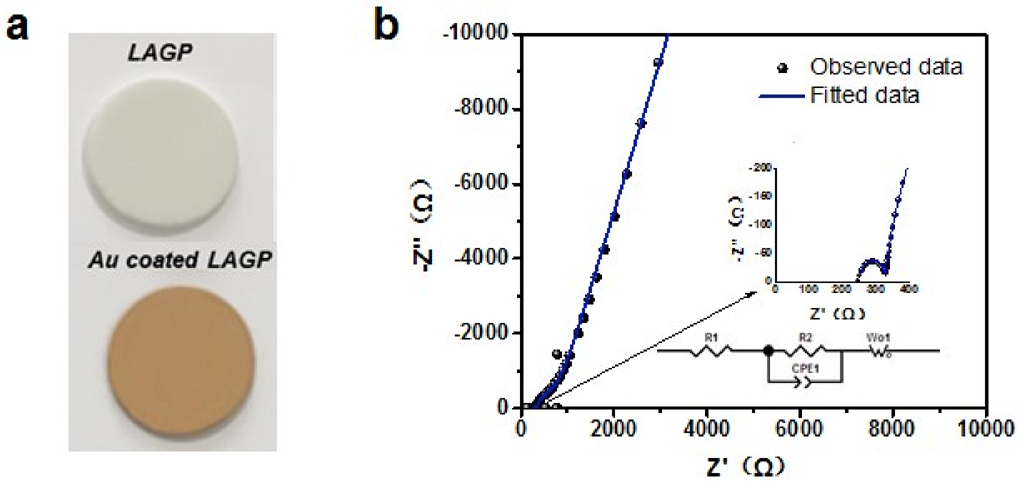

Figure S3 a) Optical image of LAGP pellet before and after coating Au film. b) The electrochemical impedance spectroscopy plots of the LAGP pellet using Au/LAGP/Au symmetric battery. The inside figure (Fig. S3b) is Nyquist plot and an equivalent circuit. The perturbation voltage is 5mV in the frequency range of 1 MHz to 0.1 Hz. In the equivalent circuit diagram, R1 is the bulk resistance; R2 is the grainboundary resistance and CPE1 is a constant phase element; Wo1 is the Warburg diffusion resistance The R1 is 251.8 Ω and the R2 is 72.3 Ω. In addition, the thickness (L) and the diameter (D) of the LAGP pellet is 0.1 cm and 1.7 cm, respectively. Final, the total conductivity of the LAGP pellet is about 3.9 × 10^{-4} S cm^{-1} according to formula (1) in which S is the surface area and R is the sum of R1 and R2.

$$\sigma = \frac{L}{S \times R} \qquad (1)$$

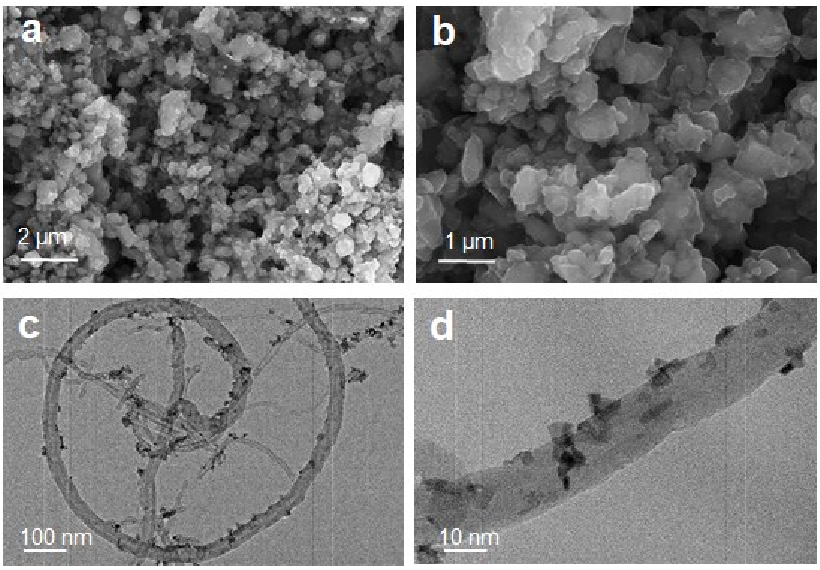

Figure S4 (a, b) SEM images of 3D air electrode (RuO_2/CNT/LAGP). (c, d) TEM images of RuO_2/CNT. Air cathode using RnO_2 and CNT as catalyst and LAGP particles as Li-ion transport medium. The complex of CNT (wall thickness ~30 nm, Fig. S4d) and RuO_2 (~

10 nm, Fig. S4d) as catalyst can significantly reduce overpotential of Li-Air battery during the cycle. The introduction of LAGP nanoparticles (~500 nm to ~1 um, Fig. S4b) could ensure an effective Li-ion transmission of the cathode even in areas beyond the LAGP ceramic membrane.

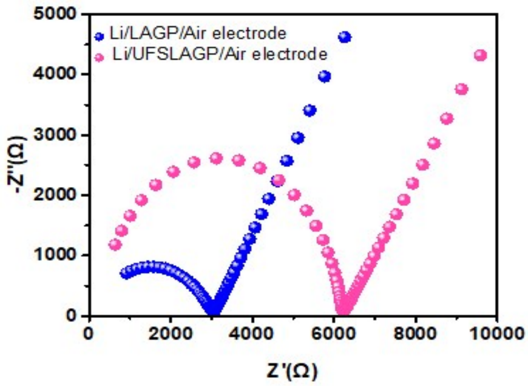

Figure S5 Electrochemical impedance spectroscopy plots of the all-solid-state Li-Air cell based on LAGP with protrusions and UFSLAGP electrolyte, respectively. Among them, the interface impedance of Li-Air battery based on LAGP with protrusions is about 6000 Ω. The interface impedance of Li-Air battery based on UFSLAGP is about 3000 Ω.

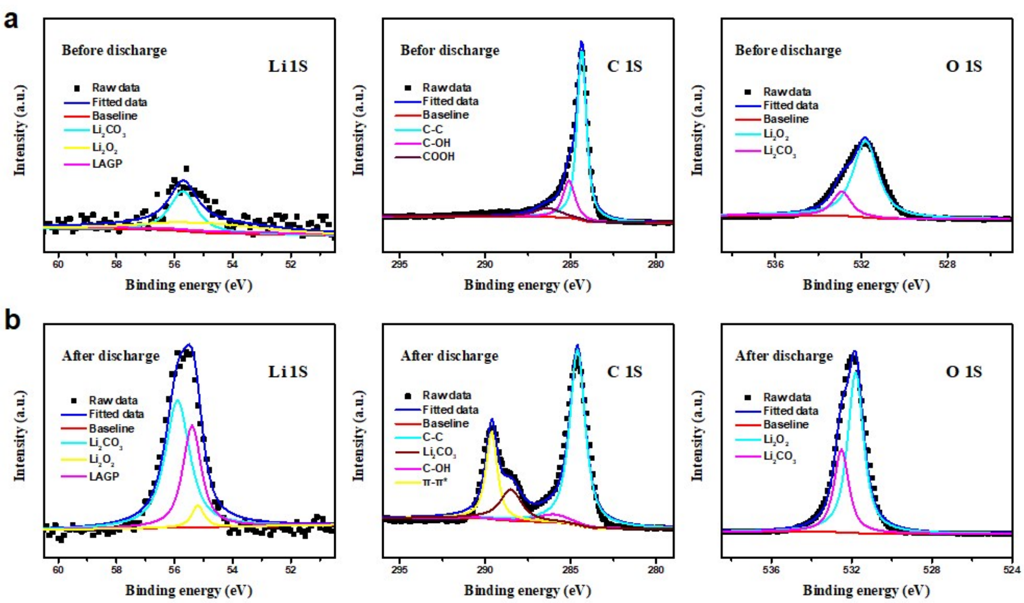

Figure S6. High-resolution XPS spectra (Li1s, C1s and O1s) of the air cathode for Li-Air battery based on LAGP with protrusions before (a) and after (b) discharge. Corresponds to the formation of the reported discharging products, including Li_2O_2 Li_2CO_3 and LiOH.

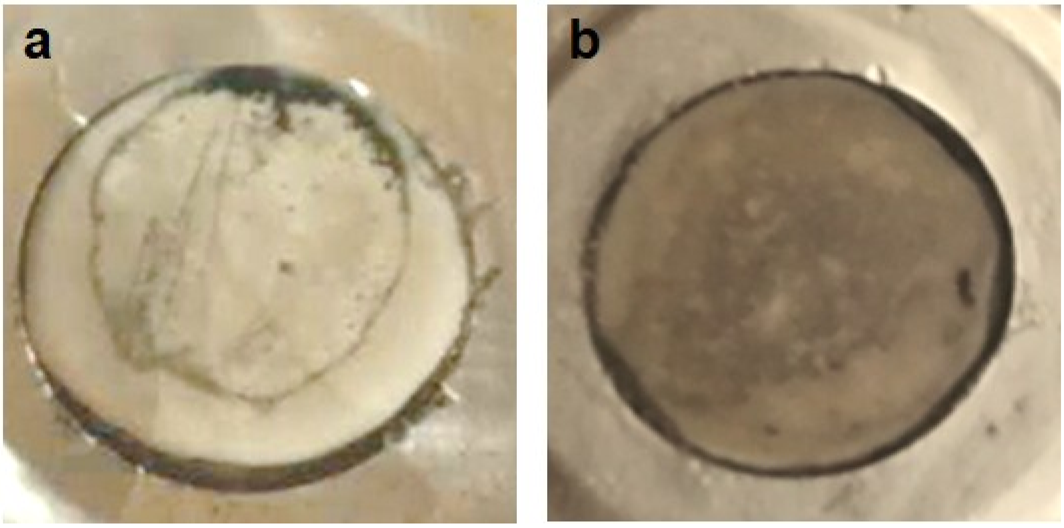

Figure S7 Optical photo of the cycled all-solid-state Li-Air battery based on LAGP with protrusions (a) and (b) UFSLAGP after removing the air electrode.

Table 1: A summary of the performances of solid-state Li-Air batteries at room temperature (RT) in the literature,[4,11,12,24,25,46] in comparison to what is achieved in this work.

Types	Electrolyte	Cathode	Current density	Capacity (mAh g^{-1})	Temperature (°C)	Cycles	Ref.
All-solid-state Li-Air battery	LAGP	CNT/LAGP	500 mAg^{-1}	1700	RT	1	4
Quasi-solid-state Li-Air battery	LATP	Pt	0.5 mA cm^{-2}	221	RT	20	46
All-solid-state Li-Air battery	Polymer film +LAGP	CNT/LAGP	10 mAg^{-1}	400	RT	1	11
All-solid-state Li-Air battery	LAGP	CNT/LAGP	400 mAg^{-1}	1000	RT	10	12
Quasi-solid-state Li-Air battery	LLZO	CNT/RuO_2/LAGP +IL	0.1 C	--	20	10	25
Quasi-solid-state Li-Air battery	LAGP	CNT/RuO_2/LAGP +IL	200 mAg^{-1}	1000	RT	9	24
All-solid-state Li-Air battery	LAGP	CNT/RuO_2/LAGP	400 mAg^{-1}	1000	RT	27	This Work