

Electronic Supplementary Information (ESI)

Facile and scalable both carbon- and binder-free electrode materials for an ultra-stable and highly improved Li-O₂ battery

Cuiping Luo,^a Jiade Li,^a Shengfu Tong,^{a*} Shiman He,^a Jun Li,^b Xianfeng Yang,^c Xiaohui Li,^a
Yuying Meng,^a and Mingmei Wu^{a*}

^a MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

^b School of Electronic Science and Engineering, Nanjing University, Nanjing 210046, China

^c Analytical and Testing Center, South China University of Technology, Guangzhou 510640, China

Address correspondence to:

Shengfu Tong, tongshf@mail.sysu.edu.cn

Mingmei Wu, ceswmm@mail.sysu.edu.cn

Experimental Section

Preparation of Ti@Ru

A plate of titanium mesh (15 mm × 15 mm, wire diameter 0.1 mm, 80 mesh, obtained from Hebei Hengshui Shengzhuo Metal Mesh Co. Ltd.) was thoroughly washed by water, acetone, 2-propanol, respectively and then dried at 70 °C. After that, the Ti mesh was annealed at 500 °C for 2 h in air and marked as A-Ti. The Ru nanoparticles were prepared through a controllable electrochemical deposition in a three-electrode system, with an Ag/AgCl (sat. KCl) and Pt wire as reference and counter electrode respectively. The aqueous electrolyte was composed of 5 mM RuCl₃, 0.5 M H₂SO₄ and 0.5 M ethylene glycol, and saturated with N₂ before electrodeposition. A potentiostatic approach was utilized throughout this research work, and the potential applied was -0.5 V (vs. Ag/AgCl) while the electrolyte was kept stillness in the N₂ atmosphere. The amount of Ru can be readily adjusted and controlled by the quantity of electric charges in the electroplated process, and various Ru loadings were studied for optimizing which were listed in Table S1 in the electronic supplementary information (ESI). After the electroplated process, the Ti@Ru mesh was thoroughly syringed with deionized water to remove the physical adsorbed reactants.

Structural and physical characterization

The structure of the materials was measured by X-ray diffraction (XRD, Rigaku, D-MAX 2200 VPC) using Cu K_α radiation, while the morphologies of the materials were characterized by scanning electron microscopy (SEM) using an FEI Quanta

400F electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were obtained on an X-ray photoelectron spectrometer (ESCALab250) for surface element state analysis.

Electrochemical measurements

CR2032-type coin cells were assembled in a glove box filled with dry Ar to measure the discharge, charge and the cycle properties in Li-O₂ batteries. The as-prepared Ti@Ru mesh was cut into wafer in diameter of 12 mm and the loading mass of Ru was shown in Table S1 (ESI). In the electrochemical testing, the specific capacity was normalized by the weight of Ru. The coin cell contained a stainless steel, a lithium foil anode, a piece of glass microfiber filter, a piece of microporous membrane and a Ti@Ru cathode. The electrolyte contained tetraethyleneglycol dimethyl ether (TEGDME) mixed with LiCF₃SO₃ in mol ratio of 4:1. The LiFePO₄ anodes were carried out by a common preparation method to assemble the full cells. We mixed LiFePO₄, acetylene black and poly(vinylidene fluoride) (PVDF) by a weight ratio of 80:15:5 and dispersed the mixture in n-methyl pyrrolidone (NMP) solvent to form a slurry. After stirring for 4 hours, the slurry was evenly pasted onto the Cu film and the anode film was dried in a vacuum oven at 120 °C overnight. The LiFePO₄ electrode mass loading is averagely 0.81 mg cm⁻². The galvanostatic charge/discharge tests were completed using a Neware battery testing system. CVs for the cells using lithium and LiFePO₄ as counter electrodes were carried out at a scan rate of 5 mV s⁻¹ in the voltage range of 2.1–4.4 V vs Li/Li⁺ and 2.0–4.4 V vs Li/Li⁺, respectively, by an electrochemical workstation (Shanghai Chenhua CHI1000C

C16061).

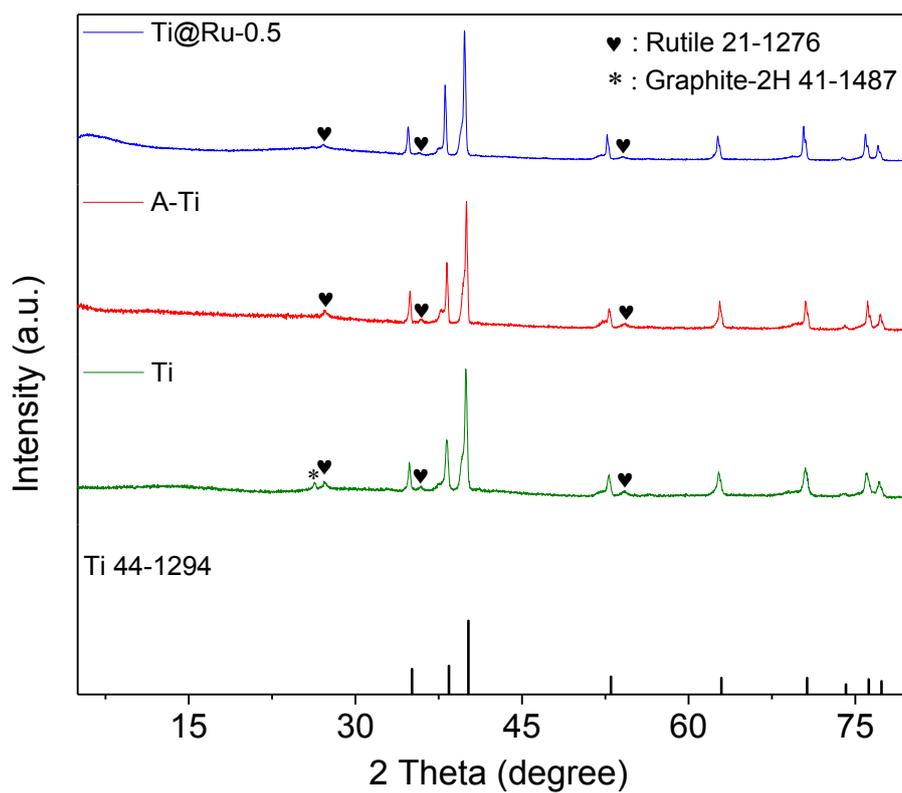


Figure S1 XRD patterns of the pristine Ti, A-Ti and Ti@Ru-0.5.

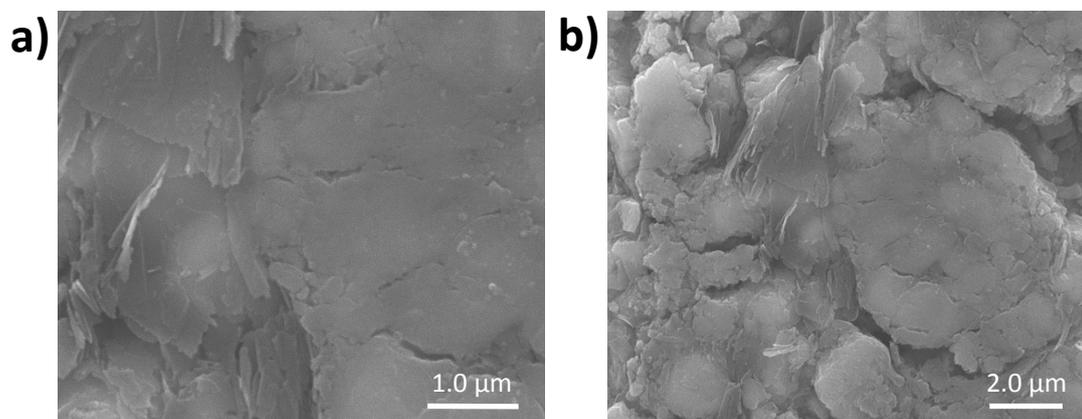


Figure S2 SEM images of bare A-Ti.

Table S1 The relationship between quantity of electric charge and amount of Ru based on the Faraday's law.

Electrode name	Work electrode		Mass of Ru on cathode (mg)
	Quantity of electric charge (C)	Ru amount of substance ($\times 10^{-6}$ mol)	
Ti@Ru-0.2	0.2	0.691	0.035
Ti@Ru-0.5	0.5	1.727	0.088
Ti@Ru-0.8	0.8	2.763	0.140
Ti@Ru-1.0	1	3.454	0.175
Ti@Ru-2.0	2	6.908	0.351

The surface area of work electrode and cathode are 2.25 cm² and 1.13 cm², respectively.

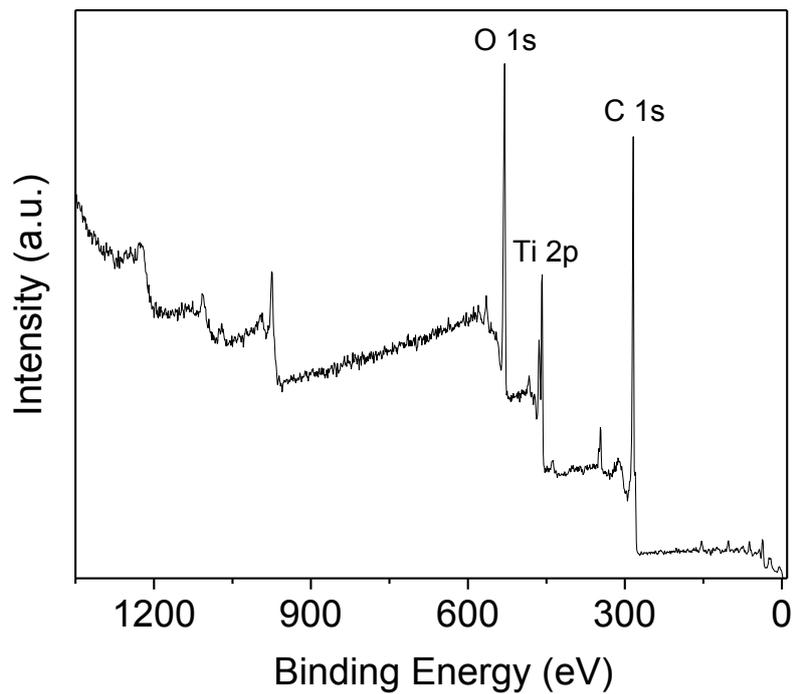


Figure S3 XPS spectrum of freshly prepared Ti@Ru-0.5.

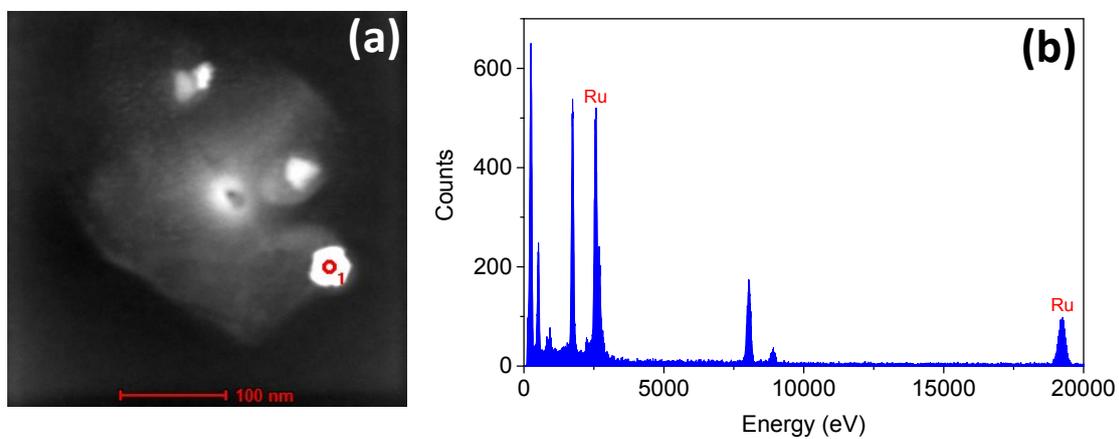


Figure S4 (a) HAADF images of the Ru nanoparticle on Ti@Ru-0.5. (b) EDS pattern of point 1 in HAADF in Figure S4a.

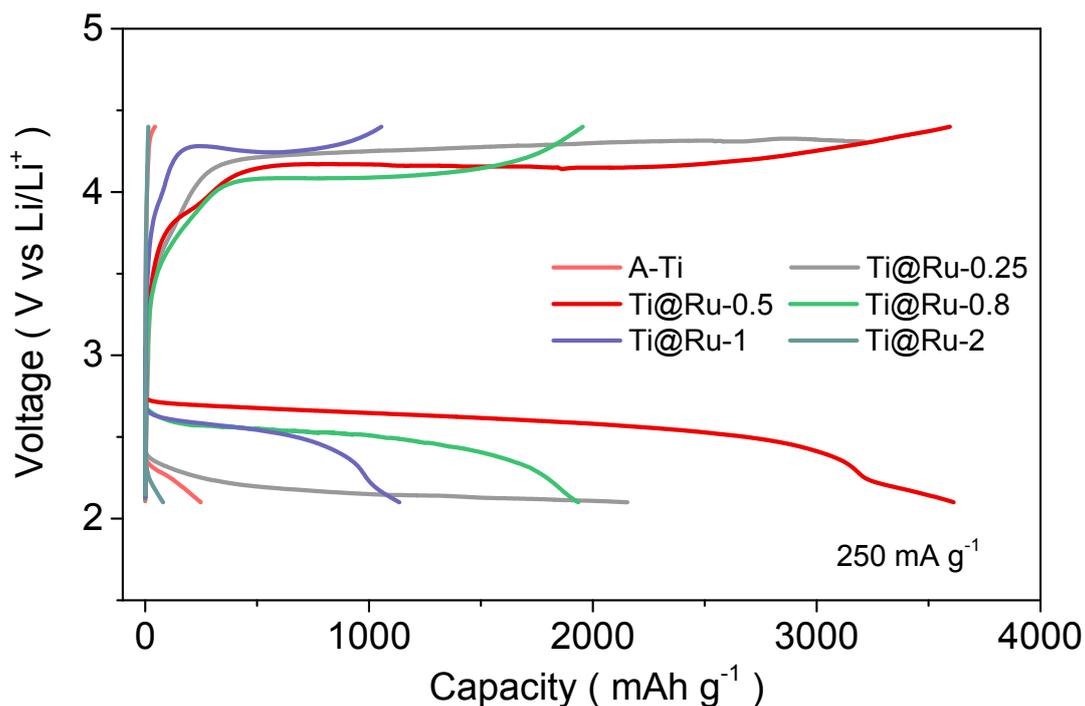


Figure S5 The first galvanostatic discharge/recharge curves of A-Ti and Ti@Ru-Q based Li-O₂ batteries at current density of 250 mA g⁻¹ (Q=0.25, 0.5, 0.8, 1, and 2). Assuming that A-Ti and Ti@Ru-0.5 have the same mass of active material.

Table S2 The specific capacities and overpotentials of bare A-Ti and Ti@Ru-Q based Li-O₂ batteries summarized from the discharge/recharge performances in Figure S5.

Sample	Specific capacity (mAh g ⁻¹)	Overpotential (V)	
		Discharge process	Charge process
A-Ti	248	0.73	>1.44
Ti@Ru-0.25	2154	0.82	1.34
Ti@Ru-0.5	3612	0.36	1.18
Ti@Ru-0.8	1934	0.43	1.12
Ti@Ru-1	1135	0.41	1.28
Ti@Ru-2	80	>0.86	>1.44

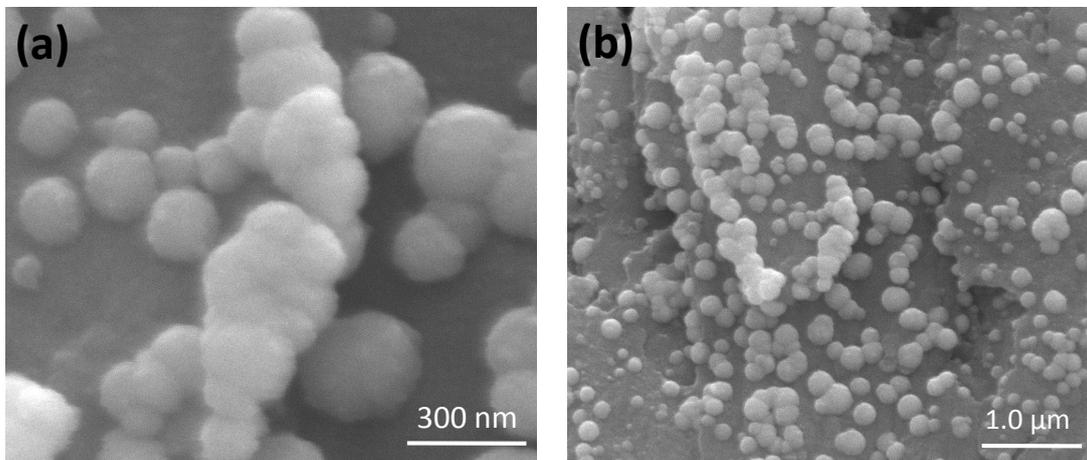


Figure S6 SEM images of Ti@Ru-2 in different magnifications.

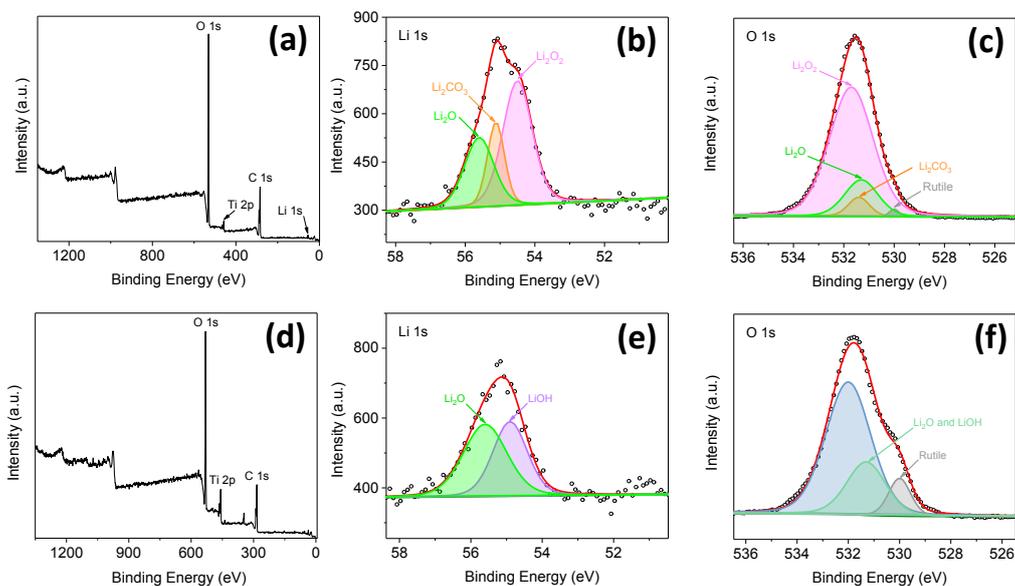


Figure S7 (a-c) XPS survey spectrum, high-resolution spectra of Li 1s and O 1s of Ti@Ru-0.5 at first discharged state, respectively. (d-f) XPS survey spectrum, high-resolution spectra of Li 1s and O 1s of Ti@Ru-0.5 at first charged state, respectively.

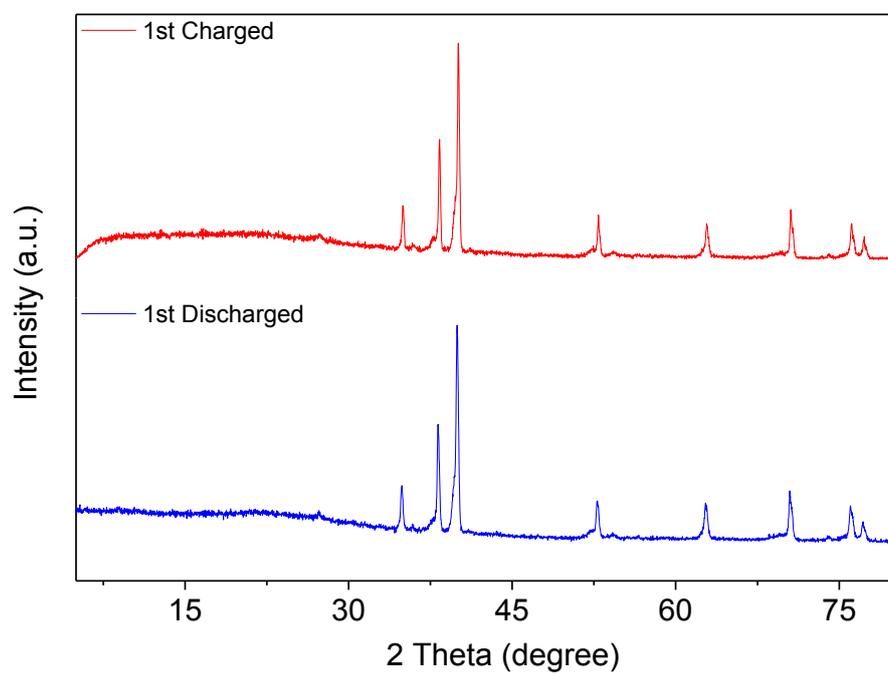


Figure S8 XRD patterns of the Ti@Ru-0.5 cathode experiencing the first discharged (blue curve) and recharged (red curve) processes.

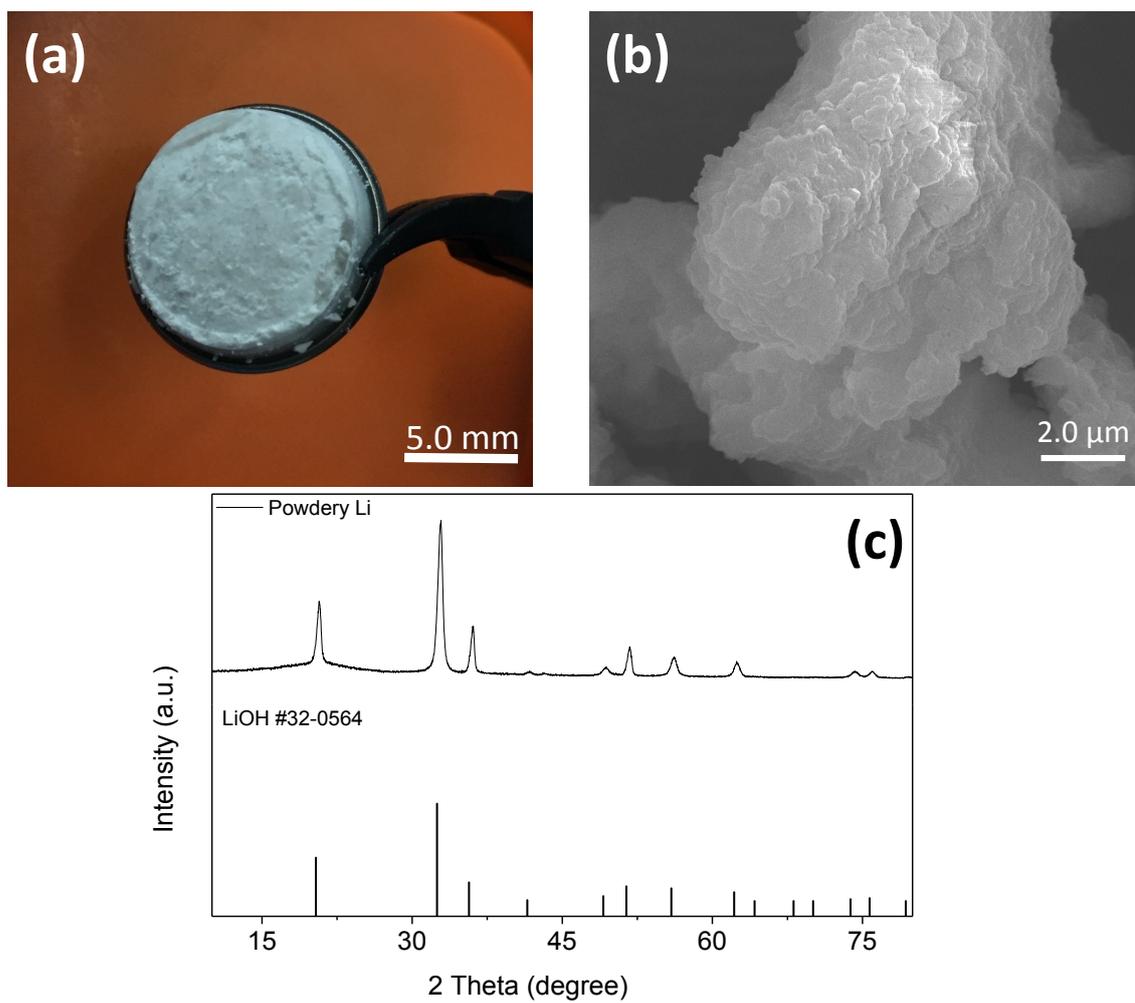


Figure S9 The digital photo (a) and SEM image (b) of the lithium foil after 100 cycles. (c) XRD pattern of the lithium foil after 100 cycles.

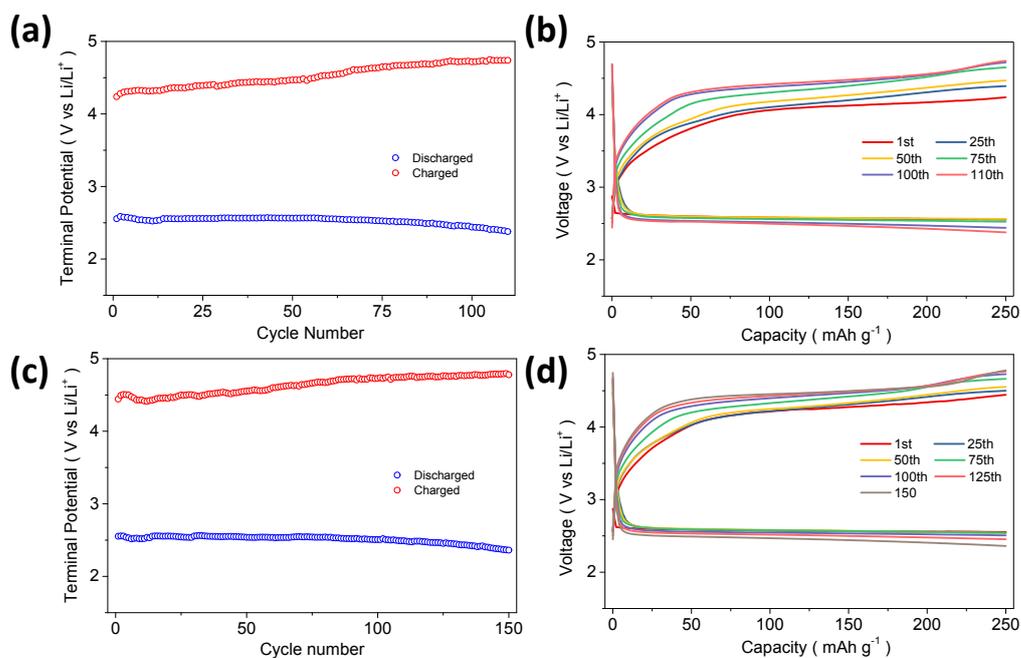


Figure S10 (a) and (c) The terminal voltages of Ti@Ru-0.5 as a function of cycle number. (b) and (d) The galvanostatic discharge/recharge curves of the Ti@Ru-0.5 based Li-O₂ battery. (a) and (b) are the performances of the initial system, while (c) and (d) are the performances of the re-assembled Li-O₂ battery with the cycled Ti@Ru-0.5 (dis-assembled from the system after the measurements shown in Figure S10a and S10b) and a fresh lithium foil.

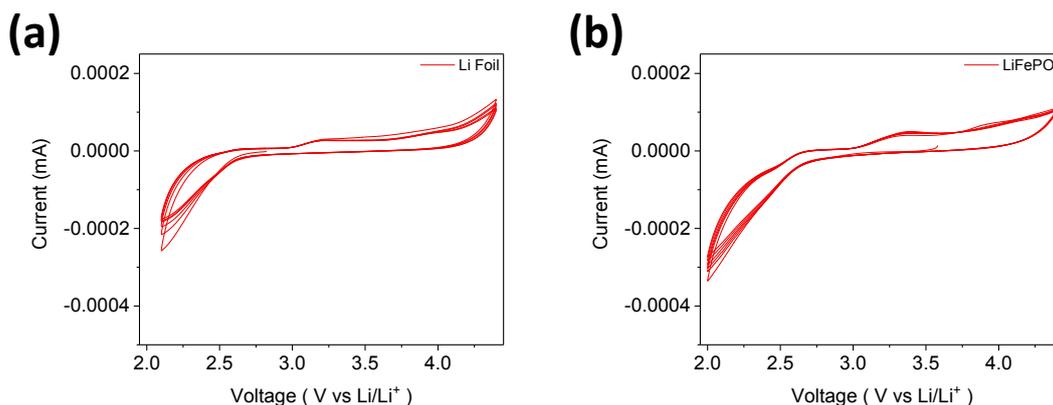


Figure S11 Cyclic voltammograms for the cells using lithium (a) and LiFePO₄ (b) as counter electrode at a scan rate of 5 mV s⁻¹.

Figure S11 shows the CVs of the cells with (a) Li foil and (b) LiFePO₄ as counter electrode, respectively. It can be seen that the shape of the curves is similar in the potential region between 2.0 and 4.4 V (vs. Li/Li⁺), similar as reported previously.^{1,2} In detail, the cathodic peak current in the potential region between 2.6 and 2.0 V is attributed to the oxygen reduction reaction (ORR), accompanying with the formation of discharge product, mainly Li₂O₂ as discussed in Figure 2, Figure S6 and S7. The anodic current peak at 3.2 and 3.5 V is ascribed to the oxidation of Li₂O₂. The broad peak at the potential more positive than 3.7 V can be arisen from the decomposition of Li₂O₂ and Li₂CO₃. These peaks agree well with the plateaus observed in the galvanostatic discharge and recharge curves as described in Figure 2a, 3a, 4b and S10. These results indicate that the LiFePO₄ can be used as reference electrode.

Notes and references

- 1 M. Safari, B.D. Adams and L.F. Nazar, *J. Phys. Chem. Lett.*, 2014, **5**, 3486-3491.
- 2 Y. Lu, S. Tong, F. Qiu, J. Jiang, N. Feng, X. Zhang, P. He, H. Zhou, *J. Power Sources*, 2016, 329, 525-529.